POLYMER SCIENCE: U.S.S.R.

VOLUME 1

1960

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PERGAMON PRESS LTD.
LONDON · OXFORD · NEW YORK · PARIS

This Journal is published by Pergamon Press for Pergamon Institute
and contains selected papers translated from *Vysokomolekuliarnye soedineniia*
Volume 1, 1959.

Vysokomolekuliarnye soedineniia

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Pergamon Press Ltd.
Headington Hill Hall, OXFORD, England
122 East 55th Street, NEW YORK 22, N.Y., U.S.A.

1961

Printed in Poland to the order of Państwowe Wydawnictwo Naukowe by Drukarnia im. A. M., Poznań

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FOREWORD

By the Editor of *Polymer Science: U.S.S.R.*

THE growth of the investigation of high polymeric systems has proceeded at an almost explosive rate in all parts of the world for a number of years. The contribution of Russian chemists and physicists in this field of scientific endeavour has been large, but has remained to a considerable extent inaccessible to Western workers. The appearance of a new Russian journal devoted to high molecular-weight compounds underlines the amount of work undertaken in the Soviet Union and, as the preface to the first number shows, the determination of the Russians to strive towards a parity with the West in this field.

It is therefore of importance that much of the original material presented in the journal should be made available to English-speaking workers. In the first instance selected papers will be published with English summaries of the remaining work: selection is intended to cover as wide an area as possible.

It is hoped that this enterprise will commend itself to all English-speaking polymer scientists.

G. M. BURNETT

Chemistry Department, University of Aberdeen

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FROM THE EDITORS*

WITH this issue we commence publication of the journal *Vysokomolekuliarnye soedineniia*, a periodical scientific organ published with the active participation of the Council for Macromolecular Compounds of the Section of Chemical Sciences of the U.S.S.R. Academy of Sciences, of a number of scientific-research institues of the U.S.S.R. Academy of Sciences and of the Academies of Sciences of associated republics, of a number of higher educational establishments and a large number of scientific-research establishments and laboratories of the industries concerned with the production processing and utilization of polymers.

The new journal takes as its main task the furtherance of the progress of our national polymer science, which at the present time is of paramount importance in the task of the rapid development of the polymer and polymer products industries and in the task of finding rational methods for the utilization of polymeric materials.

A resolution of the May Plenum of the Central Committee of the CPSU (1958), "The rapid development of the chemical industry and in particular the production of synthetic materials and articles manufactured from them to satisfy the requirements of the population and the needs of the national economy", demanded a vigorous increase in the chemical industry and set forth the task of making widespread use of polymeric materials in all fields of the national economy and culture of our country.

As an expression of the creative application and development of the Marxist-Leninist theory and of the conformity of this theory with practical communist construction, the decree of the May Plenum of the Central Committee of the C.P.S.U. constitutes an important link in a series of measures, intensively developed by the Party, to form a concrete programme of action for the realization of the historic resolutions of the 20th Congress of the C.P.S.U.

At the present time progress in any technical field is impossible without widespread utilization of chemical products and particularly of polymers, which have long since ceased to be substitutes for natural products and have become irreplaceable materials in their own right. In addition a rapid development of the synthetic polymer industry makes possible, in the shortest possible time, a sharp increase in production of goods in popular demand. And finally the utilization of polymers assists to a substantial degree in the growth of the pro-

* Vysokomol. soedin. **1**: No. 1, 3–8, 1959.

ductivity of labour — the chief requirement for a high rate of rise in the national economy, which would enable a solution of the basic economic problems of the U.S.S.R. to be brought considerably nearer, and a large step forward to be made in the creation of the material-production basis of communism.

It is for this reason that the May Plenum of the Central Committee of the C.P.S.U. placed before the whole Soviet nation the task of the rapid expansion of chemical industry, particularly in the production of synthetic, polymeric materials, a problem to which attention was drawn in the resolutions of the extraordinary 21st Congress of the Communist Party of the Soviet Union, which examined and affirmed the control figures for the development of the natural economy of the U.S.S.R. for the years 1959–1965.

In this historic document of the vigorous future improvement in the economics, culture and material prosperity of the toiling U.S.S.R., without equal in history, there are reflected the striking plans for the development of the chemical industry of our country. For the development of the chemical industry provision is made for setting aside 100–105 milliard roubles of capital investment and about half of this total assignment will be spent on the construction of undertakings for the production of plastics, artificial and synthetic fibres, synthetic rubber and other synthetic products.

In the resolutions of the 21st Congress of the C.P.S.U. attention was drawn to the necessity for the widespread development of the production of synthetic materials, including that of increasing the production of artificial fibres 4 times, of the most valuable of these (the synthetic fibres) by 12 to 14 times, and of plastics and synthetic resins by more than 7 times, during the process of fulfilling the 7-year plan.

The utilization of new raw materials is characteristic of the development of the polymer industry in the current 7-year plan. The creation of a vigorous and manifold development of the synthetic-material industry is foreseen, on the bases of the utilization of waste gases from petroleum extraction and of natural gases.

Among the measures worked out by the Presidium of the Central Committee of the C.P.S.U. and by the Soviet Ministries of the U.S.S.R., provision is made for the widespread development of scientific research on polymers, the creation of a large number of new scientific establishments, laboratories and experimental plants, the widening of the function of training of engineer-technical and scientific cadres, the organization of new publications concerned with polymers, and in particular, the publication of the present journal of the theoretical and experimental chemistry and physics of polymers *Vysokomol. soedin.* (*High-molecular Compounds*).

The tasks standing before our national polymer industry are large and important.

In developing those glorious traditions of Russian chemical thought, the traditions of the great coryphaei of science — M. V. Lomonosov, A. M. Butlerov,

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D. I. Mendeleev, N. D. Zelinskii and S. V. Lebedev — Soviet scientists have made their not insignificant contribution to the treasure-house of chemical knowledge, in the work of the establishment and vigorous development of the young polymer science, which came into existence as an independent branch of chemistry only some 20–30 years ago.

However, in the light of the tasks set forth by the extraordinary 21st Congress of the C.P.S.U. it is necessary to bring about the sharp acceleration in the future development of this branch of chemical knowledge necessary to accomplish a daring leap in this field in order that our national polymer science should take a leading position in the polymer science of the world.

In the theses of Comrade N. S. Khrushchev's report to the 21st Congress of the C.P.S.U. on the control figures for the development of the national economy of the U.S.S.R. for the years 1959–1965, unanimously approved by the delegates of this historic congress, it is directly recorded that "in the field of chemistry an important task is the all-round expansion of theoretical research, making possible the development of new, improved technological processes and the creation of synthetic materials with properties satisfying the demands of modern technology".

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We are justified in expecting from the huge collective of Soviet scientists and specialists working in the fields of polymer science and industry the opening of new approaches to the study of the processes of production of polymers and of methods of processing them, and to new ways of utilizing them. In our time of violent expansion of the polymer industry, the deficiencies in theoretical investigations, in the widespread organization of research work and in arriving at scientific generalizations from practical data are felt very keenly. Minute attention to detail, which does not keep pace with present trends, must already be regarded as a danger of ill-effective expenditure of effort and means, which does not, as a rule, lead to any substantial practical results.

We are justified in expecting the participation, in this notable field of chemistry, of scientists and specialists in physics, biology, mechanics and other branches of learning and above all, naturally, the widespread participation of chemists and workers in the various branches of chemistry.

Strictly speaking, polymer science was created as an independent branch of chemistry by the efforts of specialists in the fields of colloid, organic, inorganic and physical chemistry, by the efforts of physicists and biologists and by those of specialists in other branches of science. Only the close cooperation of scientists of various types can achieve serious successes in the progress of our national polymer science and enable the large, practical problems to be solved. Of prime importance in the task of our journal is the all-round support of the business of developing a progressive polymer science, with its new approaches and investigations, with its fulfilment of the scientific tasks involved, by scientists and specialists of various spheres of knowledge — tasks which assist in the search for a rational course of improvement in technological meth-

ods of processing polymers, which assist in the creation of new classes of polymeric compounds and which fulfil the demands of modern technology.

Development of the chemistry and physics of polymers will undoubtedly exert an effect on the advancement of medical science and of many branches of biology, particularly of biochemistry, biophysics, genetics etc. Investigation of the processes of synthesis of macromolecular compounds occurring in nature, study of their properties and structure and, in particular, work on the modelling of biological systems will give invaluable assistance to doctors and scientists in the solution of the practical problems with which they are faced, in the deep penetration of medical and biological science in the understanding of the functions of various organs of the living organism and thus finding means of restoring or changing these functions.

In virtue of the above theoretical and experimental researches on the structure and properties of natural polymers, investigations of models of biologically-active polymers and studies in the mechanism of synthesis of macromolecular compounds in nature will also be published in the journal *Vysokomol. soedin.*

We shall examine, in a general way, the chief tasks facing our national polymer science, that arise from the position of this science at the present time.

These tasks can be separated into three independent parts: the synthesis of polymeric molecules, the production of polymeric materials and articles made from them and the study of the processes occurring in polymers under the conditions and regimes to which polymeric materials and articles are subjected in use.

The whole complex of problems of both the extension of the types of low-molecular substances that can be used for the synthesis of polymers, i.e. types of monomers, and of the search for new methods and systems of synthesis of polymers from new monomers and of monomers already used for polymerization, is involved in the first task. It is quite evident that this task must be accompanied by the development and perfecting of methods of determining the size, shape and structure of the chain molecules, and also the development of a general theory of the dependence of the properties and structure of polymers on the chemical structure of the molecules of the polymeric material.

The instigation of research work, on a broad basis, on new monomers and new types of polymers is dictated by the necessity for the solution of a number of important, practical problems. One of the more fundamental of such problems is the production of polymers capable of maintaining their useful properties over the widest possible temperature range. That is, the creation of heat-resistant and low-temperature-resistant rubbers and plastics.

Here it is obviously necessary to broaden research on purely organic polymers, particularly on those with a strictly regular chain structure, on inorgano-organic polymers and on internally-complexed polymers of the chelate-compound type. It is known that in polymers with a regular chain structure the glass and softening temperature are higher than those of the same polymers of irregular

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structure, that certain polymers with aromatic groups in the chain, such as for example, poly*para*xylylene, can withstand high temperatures and that, finally, inorgano-organic polymers, for example organo-silicon polymers, and internally-complexed polymeric substances also possess similar heat-stable properties at high temperatures.

The ways mentioned above make it possible in practice to raise the heat stability of polymeric materials to 300, 400 and in the best instance to 500°C. This, of course, solves a number of important, practical problems. However, the development of modern aircraft and rocket construction and the development of the electrical industry and of other spheres of technology insistently demand the creation of polymeric materials of still higher heat stability. Evidently the fundamental solution of this problem is connected with the creation of heat-resistant, inorganic rubbers and plastics. It is necessary to organize such work on the largest possible scale and to attract to it our best inorganic chemists and specialists to ensure its success.

Again, the widespread organization of research work on new monomers, and hence on new types of polymers, is dictated by the necessity for the solution of a number of other individual problems arising from the extension of the sphere of application of articles manufactured from polymers in the various branches of our national economy. Obviously there is great practical interest in the creation of polymeric semiconductors, polymeric dyestuffs, physiologically-active polymers, polymeric fertilizers of prolonged activity, photographically-active polymers and a great number of other polymeric materials requiring for their creation specially selected monomers and polymeric molecules specifically constructed.

In another direction, the need for large-scale extension of research work on new methods and procedures for the syntheses themselves is very important in the task of solving the problems of the synthesis of polymeric materials.

In fact it is known that the discovery of the method of stereospecific polymerization and the establishment of the completely new methods of uniting different polymeric compounds into straight-chain or branched molecules (block and graft copolymers) have provided means, with striking possibilities, of producing polymeric materials with strictly chosen properties. The methods and procedures for the synthesis of polymers constitute one of the most important branches of the development of the national polymer science.

Finally, it is quite obvious that all the research mentioned on the synthesis of polymers must be accompanied by a study of the basic characteristics of the products, which determine the dependence of the properties and structure of the polymers on the chemical structure of their molecules. It is very regrettable in this connexion that out-dated traditions continue to exist, of narrow specialization of research workers who are only concerned either with the synthesis of the compounds or with the physical chemistry and physics of the polymers. Papers published on the synthesis of new polymers are much impoverished

by the absence of information even about such elementary, typical characteristics of the new polymers as molecular weights, transition temperatures, heat stability etc.

The second task with which our national polymer science is faced involves the whole complex of physical and physicochemical problems connected with the production of materials and articles made from polymers. The large-scale use of crystalline polymers with their high melting point, the processing of which involves, in a number of cases, forming polymer-based articles from molten material, the use of graft and block copolymers and making a marked improvement in the mechanical and, primarily, in the durability characteristics of a number of articles made from polymers, for example of fibres and plastics, urgently require a broad extension of structural and mechanical investigations on polymers, involving a study of the nature of the orientational state of the chains and their complexes, of the nature of the crystalline state of the polymers and of the conditions controlling the stability and changes of such structures.

In addition it is necessary to assist in every way, work on the rheology of molten polymers and the profound study of the processes of solution of graft and block copolymers, problems of great practical interest almost unexamined by investigators either in the U.S.S.R. or abroad.

The specific conditions of utilization of polymers in individual branches of technology require also a detailed study of a number of other properties of polymers, as for example, the electrical, adhesion, ion-exchange and similar properties, variations in which must again depend directly on the chemical structure of the polymer chains and on the general character of the polymeric products.

Problems connected with the development of a general theory of multicomponent systems consisting of a polymer and an active filler are of particular importance. The development of methods of attaching the polymer chains to the particles of dispersed, active filler and the elucidation of the relationships that govern means of making a marked improvement in the durability properties of such systems, are prerequisites for the creation of a rational technology of production of reinforced plastics — the materials of greatest future interest to the building industry and various other branches of the national economy.

Finally the whole complex of investigations connected with the study of processes occurring within polymers under the conditions and regimes of utilization of polymeric materials and articles, is involved in the third task. It is necessary not only to produce polymers and to prepare from them the corresponding materials or manufactured articles but also to ensure the preservation of their initial characteristics for the maximum period of service.

This complex of problems is concerned with the study of the mechanism of action of light, heat, radiation, mechanical stresses etc. on polymers.

As is known, the change of properties of a polymer as a result of the action of the above factors is connected both with the chemical nature of the molecules

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and with the effect of any additive, hence these two characteristics of the polymeric product must be taken into account when conducting such investigations.

Naturally the fulfilment of this task is closely connected with the search for rational means of stabilizing a polymer by the choice of the necessary stabilizers, which can be achieved only on the basis of a detailed study of the mechanism of the so-called ageing of polymeric products.

We have here recorded only a small part of the main problems with which the national polymer science is faced. Many of them are being solved successfully, however the extent of the problems is continuously increasing and their number is growing. A great effort of the creative forces of workers in the national polymer science is necessary in order that theoretical and experimental work in this absorbing field of scientific learning should keep pace with the vigorously developing polymer industry and the widespread application of polymeric products, i.e. for the accomplishment of the practical tasks arising from the resolutions of the 21st Congress of the C.P.S.U.

The journal of theoretical and experimental chemistry and physics of polymers — *Vysokomol. soedin.* — depends on scientific workers and specialists working in the field of macromolecular compounds, in the polymer industry and in the field of application of polymers in all spheres of the economy and culture of our country.

The following structure of the journal is planned:

(1) Scientific section (publication of original papers on the theoretical and experimental chemistry and physics of macromolecular comopunds and also scientific discussions on the individual problems of polymer science).

(2) Letters to the editors (publication of short communications not later than 2 months after receipt by the editors).

(3) Scientific chronicle (the activities of the Council for Macromolecular Compounds, of the Chemical Section of the U.S.S.R. Academy of Sciences, communications concerning congresses, conferences and scientific meetings, both in the U.S.S.R. and abroad, jubilee dates, defence of dissertations etc.).

(4) Bibliography (surveys of recent scientific literature on macromolecular compounds and reviews of new books and other publications in this field).

The editors and editorial board are firmly confident that the publication of this journal will assist the fruitful development of the national polymer science if a large, creative collective of scientists and specialists of the various spheres of scientific knowledge, working both in the field of production of macromolecular compounds, polymeric materials and manufactured articles, and in the field of their application and of the study of their role in nature, rally around the journal.

Translated by E. O. PHILLIPS

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POLYMERIZATION OF ISOPRENE WITH A BUTYL LITHIUM CATALYST*

A. A. KOROTKOV, N. N. CHESNOKOVA and L. B. TRUKHMANOVA

All-Union Scientific Research Institute of Synthetic Rubber, Institute of High-Molecular Compounds of the U.S.S.R. Academy of Sciences

(*Received* 8 *August* 1958)

THE polymerization of isoprene under the influence of various catalysts has been fairly thoroughly studied [1–4]. With two exceptions [5 and 6] there has been no paper on the polymerization of isoprene with butyl lithium.

When dissolved in certain hydrocarbons at moderate temperatures isoprene polymerizes at an appreciable rate in the presence of butyl lithium. After the monomer and catalyst solutions have been mixed there is a slight induction period followed by polymerization which proceeds at a rate between the first and second order with respect to the monomer. Since the polymerization is homogeneous a linear relationship between reaction rate and catalyst concentration would be expected. Such a relationship was found only at very low butyl lithium concentrations: at higher concentrations the reaction rate remains independent of catalyst concentration.

The existence of this relationship was confirmed experimentally at four polymerization temperatures in two series of runs, conducted independently of the other (Fig. 1 and 2). The existence of the induction period and of the complex relationship between the reaction rate and catalyst and monomer concentrations indicated that the polymerization reaction catalyzed by butyl lithium was a chain process. This relationship can satisfactorily be accounted for by assuming the polymerization reaction to be composed of the accompanying elementary reactions:

(a) a chain initiation reaction consisting in the reaction of organic lithium compounds with the monomer producing active polymerization centres:

$$RLi + M \xrightarrow{k_1} MRLi^*$$

(b) a chain growth with successive additions of monomer molecules to active centres such that active centre is retained:

$$M_iRLi^* + M \xrightarrow{k_2} M_{i+1}RLi^*$$

* Vysokomol. soedin. **1**: No. 1, 46–56, 1959.

(c) a chain termination reaction in which either intermolecular two active molecules react, or an active molecule reacts with catalyst to form stable organo-metallic compounds capable of initiating new reaction chains:

$$M_iR\text{Li}^* + M_jR'\text{Li}^* \xrightarrow{k_3} R'M_i\text{Li} + RM_j\text{Li}$$

$$M_jR\text{Li}^* + R'\text{Li} \xrightarrow{k_3} R'M_j\text{Li} + R\text{Li}$$

(d) a chain transfer reaction in which active molecules react with monomer to form stable polymer molecules and organo-metallic compounds capable of initiating fresh reaction chains:

$$M_iR\text{Li} + M \xrightarrow{k_4} RM_iH + M\text{Li}\,.$$

The latter reaction can be interpreted equally well as a chain termination reaction.

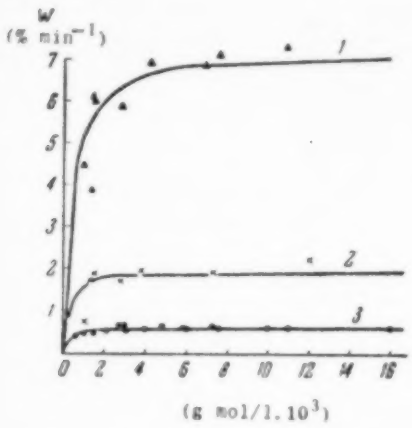


FIG. 1. Rate of isoprene polymerization in quasi-stationary period as a function of butyl lithium concentration (first series of experiments). Curve 1: 50°C, calculated for $k_2 = 220$, $k_3/k_1k_2 = 24$, $m_0 = 2{\cdot}74$ gmol/l.; curve 2: 40°C, calculated for $k_2 = 90$, $k_3/k_1k_2 = 90$, $m_0 = 2{\cdot}81$ gmol/l.; curve 3: 30°C, calculated for $k_2 = 30$, $k_3/k_1k_2 = 290$, $m_0 = 2{\cdot}90$ gmol/l.

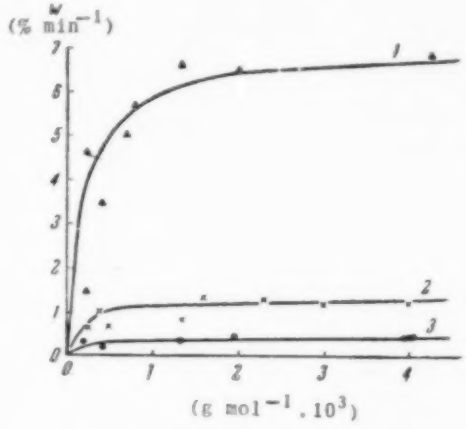


FIG. 2. Rate of isoprene polymerization in quasi-stationary period as a function of butyl lithium concentration (second series of experiments). Curve 1: 55°C, calculated for $k_2 = 420$, $k_3/k_1k_2 = 17$, $m_0 = 1{\cdot}90$ gmol/l.; curve 2: 40°C, calculated for $k_2 = 90$, $k_3/k_1k_2 = 90$, $m_0 = 1{\cdot}93$ gmol/l.; curve 3: 30°C, calculated for $k_2 = 30$, $k_3/k_1k_2 = 290$, $m_0 = 1{\cdot}94$ gmol/l.

We introduce the following symbols: m = monomer concentration; $n = [R\text{Li}] + \sum_{j=1}^{\infty} [RM_j\text{Li}]$ = organo-metallic compound concentration and $n^* = \sum_{j=1}^{\infty} [M_jR\text{Li}^*]$ = active molecule concentration.

Neglecting dissociation of the catalyst by random impurities, the combined concentration of organo-metallic compounds and active molecules during the entire process is equal to the initial catalyst concentration, i.e. $n_0 = n + n^*$. With a system of quasi-stationary composition where $k_1 nm = k_3 n^* n_0 + k_4 n^* m$, the polymerization rate W is given by:

$$W = -\frac{dm}{d\tau} = k_2 n^* m = \frac{k_1 k_2 n_0 m^2}{(k_1 + k_4)m + k_3 n_0} \tag{1}$$

At relatively high catalyst concentrations, i.e. $k_3 n_0 \gg (k_1 + k_4)m$ equation (1) reduces to

$$W = k_1 k_2 k_3^{-1} m^2 \tag{2}$$

Consequently under these conditions the polymerization rate in the quasi-stationary state is independent of the catalyst concentration and proportional to the square of the monomer concetration. In point of fact over a wide range of butyl lithium concentrations (from about 0·001 to 0·016 gmol/l.) the polymerization rate alters only slightly (*cf.* Fig. 1 and 2) and when plotted against the square of the mean monomer concentration straight lines passing through the origin are found (*cf.* Fig. 3, curves 2 and 3).

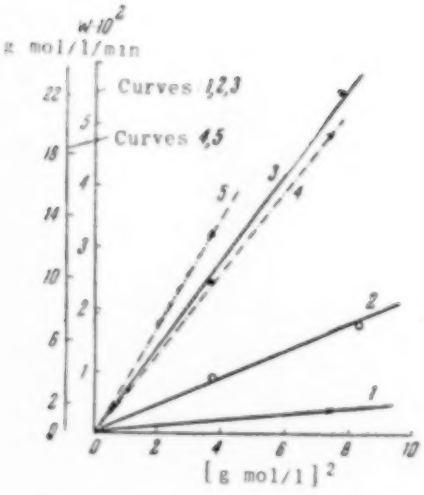


Fig. 3. Set of straight lines used to calculate value of ratio of constants: k_3/k_1k_2. Curve 1 = 20°C, 2 = 30°C, 3 = 40°C, 4 = 50°C and 5 = 55°C.

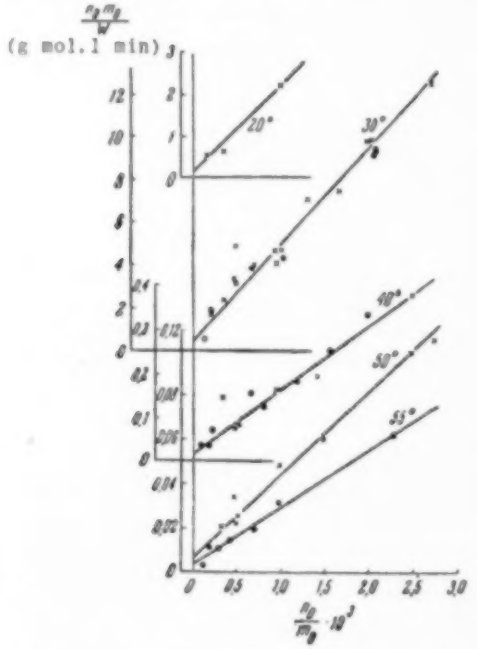


Fig. 4. $n_0 m_0/W$ plotted against n_0/m_0. Points: X = first series, ● = second series of experiments.

At low catalyst concentrations, when $k_3 n_0 \ll (k_1+k_4)m$, equation (1) becomes:

$$W = k_1 k_2 (k_1+k_4)^{-1} n_0 m \,. \tag{3}$$

With isoprene $k_3 n_0 \ll (k_1+k_4)m$ only at very low butyl lithium concentrations and it was found impossible to obtain reproducible rates so that equation (3) has not been verified experimentally.

Equation (1) can be written in the following form:

$$\frac{1}{W} = \frac{1+k_4/k_1}{k_2}\,\frac{1}{n_0 m} + \frac{k_3}{k_1 k_2}\,\frac{1}{m^2}\,. \tag{4}$$

Because $k_4/k_1 \ll 1$ it can be neglected in the first term of the equation, whence

$$\frac{n_0 m}{W} = \frac{1}{k_2} + \frac{k_3}{k_1 k_2}\,\frac{n_0}{m}\,. \tag{5}$$

Plots of $n_0 m_0/W$ against n_0/m_0 are good straight lines from whose slopes (Fig. 4) it was possible to determine values for k_2, k_3/k_1k_2 and k_3/k_1 (see Table 1).

In calculating the constants we took as the mean polymerization reaction rate the rate for the conversion of isoprene from 0·1 to 0·3 m_0 and correspondingly 0·8 m_0 as the mean monomer concentration. The curves in Fig. 1 and 2 have been plotted from the values found for the constants.

TABLE 1. VALUES OF CERTAIN KINETIC CONSTANTS

Constants	Nos. of figs. used for calculations	Temperature (°C)				
		20	30	40	50	55
$k_3/k_1 \cdot k_2$	3	1220	296	93	25	19
$k_3/k_1 \cdot k_2$	4	1300	279	92	24	16
k_2	4	10·4	30·5	89·5	221	418
k_3/k_1	5	120	96	78	65	59

The apparent activation energy of the growth reaction, E_2, is $19{\cdot}7 \pm 2$ kcal/gmol, the exponential factor in the Arrhenius equation $(5{\cdot}0 \pm 0{\cdot}4) \times 10^{15}$ and the difference in the activation energies $E_3-(E_1+E_2)$ is $-23{\cdot}5$ kcal/gmol (Fig. 5). Hence the activation energy of the chain initiation reaction exceeds by 3·8 kcal/gmol that of the chain termination reaction, thereby determining the high value of constant k_3 relative to k_1. For the initiation reaction the exponential factor is greater than for the termination reaction by a factor of only 5. The values for the constants k_1 and k_3 are usually determined separately from the experimental results of the mean mol. wt. in terms of the catalyst or monomer concentration.

Here this procedure is inadmissible since the high-molecular organo-metallic compounds that form during the chain termination reaction provide new polymerization centres. The presence of the termination reaction merely causes the growth reaction to become irregular or spasmodic. After being activated by interacting with the first monomer molecule, the original organo-metallic compound soon adds a small number of monomer molecules and is de-activated to form a new organo-metallic compound. After a certain time this new molecule is activated anew, adds more monomer molecules, is de-activated and thus the cycle continues. This irregular growth process is perpetuated until all the monomer has been consumed or the active polymer molecule reacts with the monomer by a chain transfer reaction mechanism.

Thus the mean MW of the polymer formed and also the MW distribution should not differ from the corresponding values for a polymer that would be obtained by the polymerization of isoprene in the absence of one of the elemen-

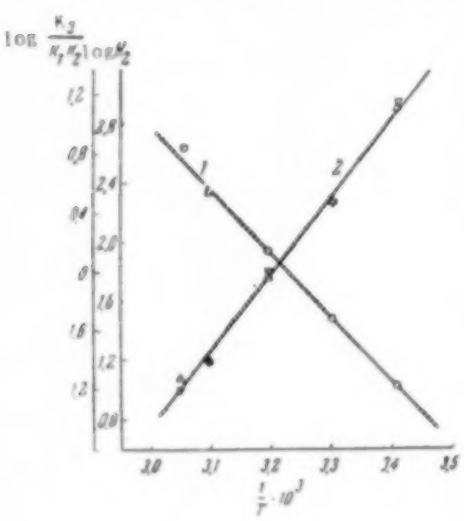


FIG. 5. $\lg k_2$ (curve 1) and $\lg k_3/k_1k_2$ (curve 2) plotted against the reciprocal of the absolute temperature.

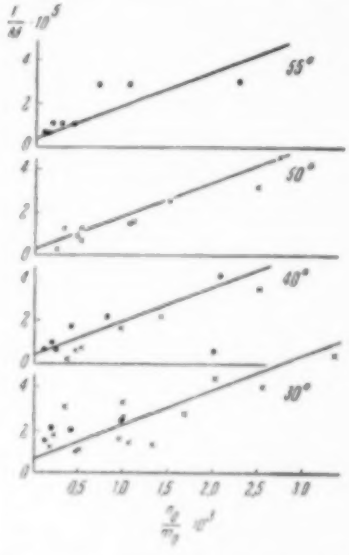


FIG. 6. Reciprocal of polymer MW plotted against ratio of initial concentrations of butyl lithium (n_0) and isoprene (m_0) for four temperatures; points: X = first series, ● = second series of experiments.

tary reactions, e.g. the termination reaction. The mean MW must obviously equal the weight of the polymer formed divided by the total number of molecules of the catalyst in question and the number of inert polymer molecules formed by the chain transfer reaction. The number of inert polymer molecules can be calculated as follows:

the rate of formation of inert molecules (p) is given by $dp/d\tau = k_4 n^* m$, and the rate of polymerization by $-dm/d\tau = k_2 n^* m$, therefore $dp/dm = k_4/k_2$. Integration gives $p = k_4(m_0 - m)/k_2$. The mean MW of the polymer formed upon completion of the reaction ($m = 0$) will be:

$$M_r = \frac{68\, m_0}{n_0 + k_4 m_0/k_2} \quad \text{or} \quad \frac{68}{M_r} = \frac{n_0}{m_0} + \frac{k_4}{k_2}$$

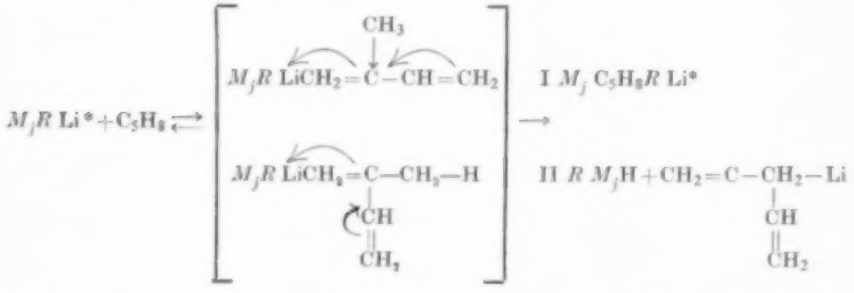
(assuming all the catalyst is used).

The points are somewhat scattered but the slopes of the best straight lines of Fig. 6 satisfy the condition that when $k_4/k_2 = 0$ the equation

$$\frac{1}{M_r} = \frac{1}{68}\,\frac{n_0}{m_0}$$

is valid. The fact that the points are widely spread is governed by two main factors: errors in measuring out the catalyst due to varying amounts of impurity, and in determining the characteristic viscosity of the polyisoprene. When isoprene is polymerized at 30°C the chain transfer rate constant, and thus the reaction rate, is less by a factor of about 2000 than the growth rate. As the polymerization temperature rises the specific value of the chain transfer reaction decreases quite considerably (at 50°C the ratio $k_2/k_4 \approx 5000$) because the activation energy of the chain transfer reaction on the monomer is about 9 kcal/gmol less than that of the chain growth reaction. This low value for the constant k_4 with respect to k_2 is determined solely by the low (about 10 orders of magnitude) exponential factor.

Consequently, the second of the two competing reactions



although it has the less activation energy is very much slower because of steric hindrance. The first reaction is accompanied by the liberation of heat, 15·5 kcal/gmol, but the second is probably athermic.

Since the transfer reaction is not a dominant factor and k_1 differs by two or three orders of magnitude from k_2, the MW distribution of the resulting isoprene polymer must be very restricted (approximately Gaussian). Thus the number and weight average molecular weights shall coincide. In a number of

experiments the mean osmotic MW and the mean viscosity MW were measured (Table 2). The agreement between these values suggests the polyisoprene is extremely homogeneous.

TABLE 2. MEAN VISCOMETRIC AND MEAN OSMOTIC MOL. WT. VALUES OF POLYMERS FROM THE FIRST SERIES OF EXPERIMENTS

No. of expt.	14	13	10	4	1
Viscometric mol. wt. (thousands)	955	64	345	121	69
Osmotic mol. wt. (thousands)	630	50	322	134	77
Polymerization temperature	40	40	50	50	50

The content of 1,2 and 3,4 isoprene groups (between 5 and 7%) is independent of the polymerization temperature and of the initial catalyst and monomer concentrations.

Hitherto the polymerization reaction of diethylene hydrocarbons with organo-metallic compounds of alkali metals has been considered to proceed by a stepwise mechanism [7 and 8]. Our relationship between the reaction rate and the initial butyl lithium concentration seems at first glance as though it can be explained by the occurrence of a dimerization of the organo-metallic compounds in solution [9 and 10]. On the basis of a stepwise reaction mechanism the polymerization process would be as follows: only monomeric organo-metallic molecules formed either by spontaneous dissociation of a dimeric type (a) or by reaction with isoprene (b) can participate in the polymerization:

$$(R_2\text{Li})\text{Li} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\,R\text{Li} \qquad \text{(a)}$$

$$(R_2\text{Li})\text{Li} + M \xrightarrow{k_1'} R\text{Li} + RM\text{Li} \qquad \text{(b)}$$

The growth of the polymer chains consists in the stepwise addition of isoprene molecules to form at each step a new organic lithium compound:

$$RM_j\text{Li} + M \xrightarrow{k_3} RM_j + \text{Li}$$

The chain termination reaction is a dimerization:

$$RM_j\text{Li} + RM_s\text{Li} \xrightarrow{k_5} (RM_j\text{Li}\,RM_s)\text{Li}$$

In the case of reaction (a) the concentration of monomeric organo-lithium compound is found from

$$K = \frac{[LiR]^2}{[(R_2Li)Li]}$$

or, in the case of reaction (b), from

$$k_1'[(R_2Li)Li]\,[M] = k_3[LiR]^2$$

because $n_0 = n + 2\,[(R_2Li)Li]$ where $n = [LiR]$.

Accordingly the polymerization reaction rate in the first case will be:

$$W = k_2 nm = 1/4\; k_2 Km \left\{ \left(1 + 8n_0/K \right)^{\frac{1}{2}} - 1 \right\}$$

and in the second

$$W = \frac{k_1 k_2 m^2}{4k_3} \left\{ \left(1 + \frac{8k_3 n_0}{k_1' m} \right)^{\frac{1}{2}} - 1 \right\}$$

For large values of n_0 when $\left(8n_0/K\right)^{\frac{1}{2}} \gg$ or $\left(8k_3 n_0/k_1' m\right)^{\frac{1}{2}} \gg 1$, the equations become

$$W = 0 \cdot 707\, k_2 K^{\frac{1}{2}}\, n_0^{\frac{1}{2}}\, m$$

and

$$W = 0 \cdot 707\, k_2 \left(\frac{k_1' n_0}{k_3} \right)^{\frac{1}{2}} n^{3/2}.$$

Thus at high catalyst concentrations the polymerization rate would be proportional to the square root of the catalyst and monomer concentrations. Our experimental findings from a sample polymerization of isoprene with butyl lithium are further proof that the polymerization reactions of diethylene hydrocarbons with organo-metallic compounds and, of course, with alkaline metals are reactions with a complex catalytic mechanism and not stepwise polymerization reactions that constitute a simple organo-metallic synthesis.

EXPERIMENTAL

A dilatometric technique was used in studying the polymerization kinetics of isoprene. The polymerization ampoule was composed of two vessels (volume 40–50 ml) joined by a tube graduated in 0·1–0·2 ml and separated by a thin glass diaphragm at the base of one of the vessels. After one of the vessels forming the ampoule had been heated at 200–250°C *in vacuo* (residual pressure 2–5 mm) for 2–4 hr it was filled by means of condensation with about 20 ml of carefully purified solvent (in the first series of experiments benzene was used and in the second, *n*-hexane) and 10 ml of isoprene, then disconnected from the ampoule-filling device. Final purification of the solvent and the isoprene took place by successive double distillation with butyl lythium. Analysis with maleic anhyd

ride showed the technical-grade isoprene to contain 99·8–99·9 per cent of isoprene. The requisite amount of butyl lithium solution in benzene (first series) or in *n*-hexane (second series) was introduced into the second vessel of the ampoule after it too had carefully been heated *in vacuo*. The vessel was then disconnected. The butyl lithium solution was formed by the direct action of metallic lithium on butyl chloride in a suitable solvent. The butyl lithium content in the solution was determined by double titration [11].

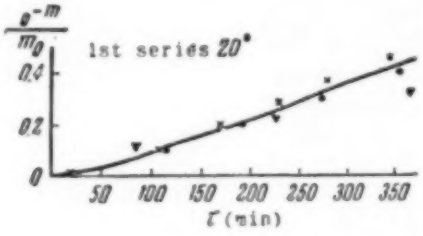


FIG. 7. Kinetic curves for first series of experiments at a reaction temperature of 20°C. Initial butyl lithium concentration (gmol/l.$^{-1} \times 10^3$): ▼=0·6, X=1·0, ●=3·0

After the contents of the ampoule had attained the thermostatically set temperature by agitation or by stirring by means of an electromagnet inside the ampoule, the diaphragm was broken, the isoprene and butyl lithium solutions mixed and note taken of the time and of the level of the original volume of the mixed solutions. Polymerization continued until almost all the isoprene had been consumed. The decrease in volume was measured with an accuracy of $\pm$2–4 per cent (relative). The mean MW of the polymer was determined by averaging over four viscometric measurements. In a number of experiments of the first series the mean osmotic MW of the resulting polymer was ascertained (Table 2). The mean MW was calculated by the formula: $\log M = 5{\cdot}00 + 1{\cdot}162 \log [\eta]$. With certain experiments the total content of 1,2 and 3,4 isoprene groups was determined by infra-red spectroscopy in the higher frequency [12] (first series of experiments) or lower frequency [13] bands of the spectrum (second series of experiments). The kinetic curves are plotted in Fig. 7–14.

CONCLUSIONS

(1) The polymerization kinetics of isoprene with a butyl lithium catalyst in a saturated hydrocarbon solution are studied.

(2) The reaction mechanism consists of a chain reaction in which the active centres are complexes of organo-metallic compounds and monomer-polymer molecules.

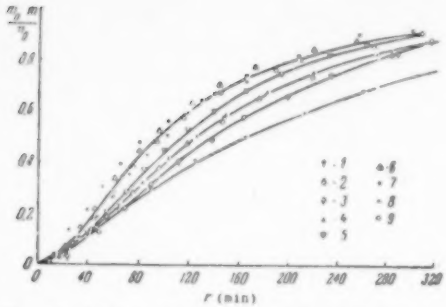


FIG. 8. 30°C : (1) 0·6; (2) 1·0; (3) 1·5; (4) 1·5; (5) 2·1; (6) 2·7; (7) 2·9; (8) 3·0; (9) 4·8.

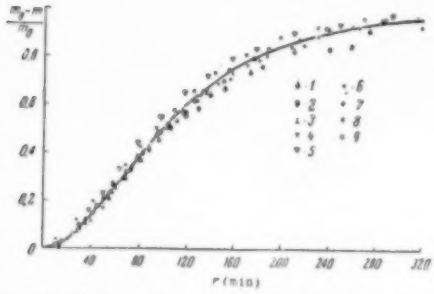


FIG. 9. 30°C : (1) 3·1; (2) 4·0; (3) 5·9; (4) 6·0; (5) 7·3; (6) 7·6; (7) 10·0; (8) 11·0; (9) 16·0.

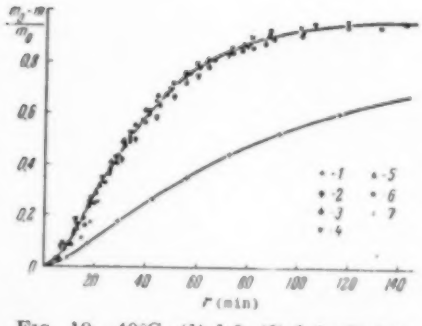


FIG. 10. 40°C : (1) 1·0; (2) 1·4; (3) 1·5; (4) 2·8; (5) 3·8; (6) 7·3; (7) 12·0.

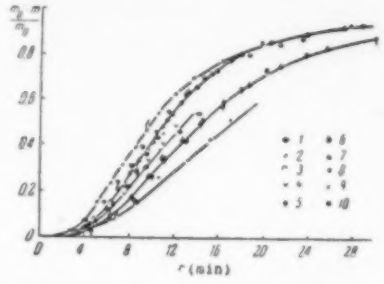


FIG. 11. (See Fig. 7) 50°C : (1) 0·9; (2) 1·3; (3) 1·5; (4) 1·5; (5) 2·9; (6) 3·1; (7) 4·2; (8) 6·9; (9) 7·1; (10) 11·0.

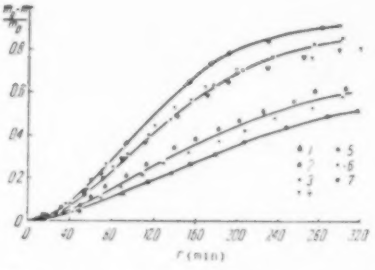


FIG. 12. Kinetic curves for second series of experiments at a reaction temperature of 30°C. Initial butyl lithium concentration (gmol/$l^{-1} \times 10^3$). (1) 0·2; (2) 0·4; (3) 1·3; (4) 1·9; (5) 4·1; (6) 4·1; (7) 4·2.

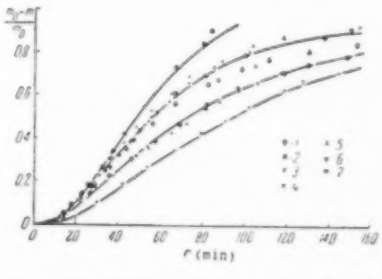


FIG. 13. 40°C: (1) 0·2; (2) 0·4; (3) 0·5; (4) 1·3; (5) 1·6; (6) 2·3; (7) 4·0.

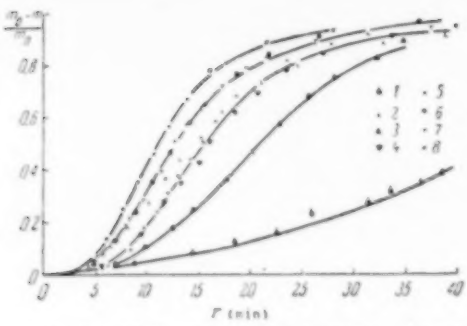


FIG. 14. 40°C: (1) 0·2; (2) 0·4; (3) 0·5; (4) 1·3; (5) 1·6; (6) 2·3; (7) 4·0.

(3) The chain growth is terminated by the active centres reacting with each other or with original organo-metallic compounds. The new organo-metallic compounds of high MW are capable of becoming polymerization centres.

(4) The resulting polymer has a narrow molecular weight distribution and the MW of the polymer upon completion of polymerization is inversaly proportional to the catalyst concentration.

(5) The microstructure of the polymer (content of 1,2 and 3,4 isoprene groups) is independent of the polymerization temperature, catalyst concentration and monomer concentration.

Translated by G. CAMERON

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THE INTERACTION BETWEEN TETRAMETHYL THIURAM DISULPHIDE AND RUBBER AND COMPOUNDS CONTAINING AN ACTIVE HYDROGEN ATOM IN THE MOLECULE*

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(*Received* 15 *May* 1958)

IN our previous communication we put forward a number of ideas relating to vulcanization with thiuram in the presence of various metal oxides [1]. Opinion is divided on the mechanism underlying the vulcanizing action of thiuram-type accelerators. Some workers [2] maintain that these accelerators owe their vulcanizing action to the liberation of active sulphur and simultaneous decomposition into simpler compounds. Others [3] have elaborated the theory that vulcanization with thiuram operates via free radicals.

Schele *et al.* point out in their papers that when vulcanization is carried out in the presence of zinc oxide, the thiuram is converted to zinc dithiocarbamate (66·6 mole per cent); it forms no other conversion products. These authors hold that an intermediate compound of thiuram and rubber is formed on the surface of the zinc oxide crystals which then decomposes to yield zinc dithiocarbamate and form chemical cross-links between the rubber molecules [4]. They fail to consider vulcanization in the absence of metal oxides and to submit their experimental findings on the direct interaction between thiuram and rubber.†

1. THE INTERACTION BETWEEN TETRAMETHYL THIURAM DISULPHIDE (TMTD) AND RUBBER

Under vulcanization conditions (at 143°C under compression) tetramethyl thiuram disulphide (TMTD) becomes added to the rubber, this being indicated by the presence of sulphur and nitrogen (incapable of removal by extraction with hot and cold acetate, cold ethyl acetate or boiling alcohol).

The kinetics governing the addition of the sulphur and nitrogen from the

* Vysokomol. soedin. **1**: No. 1, 58–67, 1959.

† After this paper reached the editorial staff of this journal a paper appeared by Schele and Hummel (Kautschuk und Gummi, 11, 1958), dealing with this point (Proofreader's note).

TMTD to the rubber are represented in Fig. 1. Attention is drawn to the fact we noted earlier [1], notably the existence of a clearly defined maximum of the kinetic curves that characterize the sulphur content in the vulcanizate. An explanation for this interesting phenomenon will be given below.

As was demonstrated by one of our number [5] the process appears to proceed by the formation of free TMTD radicals that interact with the polymer molecules of the rubber and initiate polymerization in a similar manner to the case with dibenzo thiazyl disulphide.

The unequal amounts of added sulphur and nitrogen (in per cent of the original content in the TMTD) (*cf.* Fig. 1) indicate both a symmetrical and an asymmetrical, dissociation of the TMTD into radicals in accordance with the scheme:

$$(CH_3)_2NC(S)SSC(S)N(CH_3)_2 \rightleftarrows 2(CH_3)_2NC(S)S^{\bullet}$$

(I)

$$(CH_3)_2NC(S)S^{\bullet} + {}^{\bullet}CN(CH_3)_2$$

(II) (III)

When the active hydrogen atom in the α-position with respect to the double bond of the rubber molecule breaks away radicals (I) and (II) form dithiocarbamic acid that either decomposes into carbon disulphide and amine, or is bound in the form of dithiocarbamates. The combining of the reaction products occurs in the presence of zinc oxide, lead oxide (PbO) and nickelous oxide (NiO); decomposition takes place in the absence of these oxides and with magnesium and

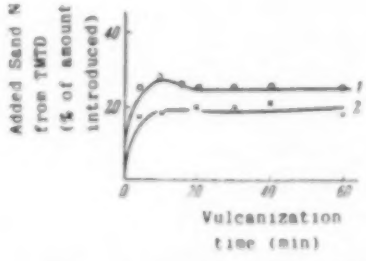


Fig. 1. Addition of sulphur and nitrogen from TMTD (in per cent of amount introduced) during vulcanization process of synthetic polyisoprene rubber (SPR). Composition of mixture (parts by weight): SPR = = 100, TMTD = 5, ZnO = 5, stearic acid = 1. 1 = sulphur, 2 = nitrogen.

calcium oxides. The stearates of these metals behave in the same manner. We shall deal separately with lead and nickelous oxides. When natural rubber is vulcanized with three parts by weight of TMTD and amounts of PbO and NiO equivalent to five parts by weight of ZnO no cross-

links are formed, i.e. the "vulcanizates" are completely soluble in xylene. The sulphur content in the extracted specimens differs little from the total sulphur content introduced by the thiuram (85–95 per cent). Extraction was effected with cold and boiling ethyl acetate and hot acetone, i.e. substances in which dimethyl lead and nickel and diethyl dithiocarbamates are sparingly soluble. We may therefore conclude that lead and nickel dithiocarbamates are present in the rubber in the combined state (perhaps as complex compounds). In vulcanizates of technical-grade, synthetic polyisoprene rubber the degree of cross-linking is less with these oxides than in the absence of metal oxides and, furthermore, it decreases inversely with the amount of lead or nickelous oxide. These details show that the combining of the reaction products of TMTD and rubber with lead and nickelous oxides is accompanied by the addition of the dithiocarbamates of these metals to the rubber chain molecules at the position of the reaction with the TMTD.

Zinc dithiocarbamate (Zn DTC) is present in the rubber in the dissolved state and can be removed by extraction. In vulcanizates not containing these metal oxides or which contain magnesium and calcium oxides the dithiocarbamic acid is not combined and decomposes to yield carbon disulphide and dimethyl amine. These two compounds are formed by qualitative reactions both singly and together (the formation of a brown precipitate of copper dimethyl dithiocarbamate upon addition of a $CuSO_4$ solution to an aqueous vulcanizate extract). Furthermore there is a considerable reduction in the over-all amount of sulphur in the vulcanizates as a consequence of the liberation of carbon disulphide. The dimethyl amine was determined quantitatively by heating a mixture of natural rubber and TMTD in the absence of metal oxides and without pressure in volatile substances (by absorption of O·1*N* HCl followed by titration of the excess with O·1*N* NaOH). The dimethyl amine reacts partly with the carbon disulphide on the condenser walls during distillation to form dimethyl amine dimethyl dithiocarbamate.

$$(CH_3)_2NC\,SH \cdot HN(CH_3)_2$$
$$\|$$
$$S$$

In the presence of zinc oxide (or zinc stearate) an extremely dense space lattice (in comparison with other metal oxides) emerges and reversion of vulcanization does not occur. The physical-mechanical properties of vulcanizates secured from polyisoprene rubber with zinc oxide surpass by far those of vulcanizates prepared with an equivalent amount of magnesium oxide (Fig. 2).

The behaviour that distinguishes zinc oxide from the other studied metal oxides in vulcanization with thiuram can be accounted for by the combination of the dithiocarbamic acid in the form of a zinc salt that is adequately stable under the vulcanization conditions and does not interact with the rubber. The kinetics of its accumulation are plotted in Fig. 3. The ZnDTC was determined

in alcohol extracts of the vulcanizates by conductometric titration [3]. The number of cross-links were determined by measuring the optimum swelling in xylene and calculated by means of the Shvarts nomograms [6]. Calculation

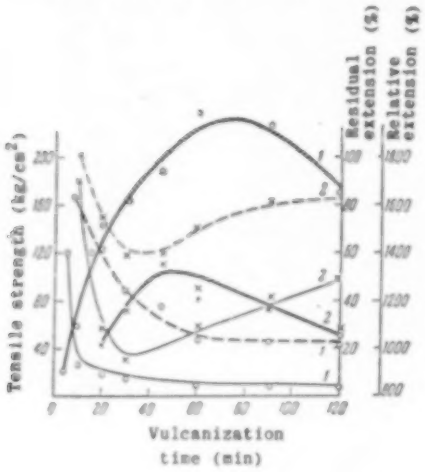


Fig. 2. Physical-mechanical properties of vulcanizates of SPR with TMTD. Compositions of mixtures (parts by weight): 1 : SPR = 100, TMTD = 3, ZnO = 1, phenyl β-naphthyl amine = 1. 2 : SPR = 100, TMTD = 3, MgO = 0·5, phenyl β-naphthyl amine = 1. ——— tensile strength, ———— relative extension, – – – – – – – residual extension.

of the number of ZnDTC molecules to one cross-link (Table 1) shows that in the initial vulcanization period the accumulation of this compound outstrips the formation of cross-links. Our results do not, therefore reflect complete identity of these two reactions as maintained by Schele *et al.* [4].

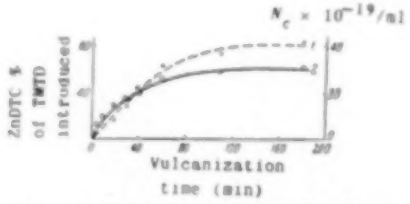


Fig. 3. Formation of cross-links (1) and zinc dicarbamate (2) during vulcanization of rubber with TMTD. Composition of mixture: extracted with cold acetone in a stream of nitrogen for 50 hr. Natural rubber (NR) = 100, TMTD = 4, ZnO = 5, phenyl β-naphthyl amine = 1.

We must point out that ZnDTC is not formed on rolling the mixtures or no extracting them with boiling alcohol (for 2 hr) because it is not present in extracts of the crude mixtures but the quantity of extracted TMTD corresponds to that introduced into the mixture.

The reaction of rubber with TMTD is largely determined by the proportion of structural units of the 1,4 and 1,2 type in the rubber. As Fig. 4 shows the

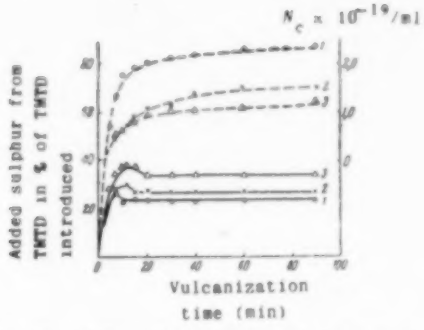


FIG. 4. Addition of sulphur from TMTD (in per cent of TMTD introduced) and formation of cross-links (N_c) on vulcanization of rubbers with different content of 1,4 and 1,2 structural units.

$\frac{S_{added}}{S_{introd.}}$; ..... N_c

Composition of mixtures (parts by weight); rubber = 100, TMTD = 4, ZnO = 5, stearic acid = 2, phenyl β-naphthyl amine = 1. 1 = natural rubber (NR) (100 per cent of 1,4 links), 2 = synthetic butadiene rubber (SKBM) (65 per cent of 1,4 links), 3 = synthetic butadiene rubber (SKB) (30 per cent of 1,4 bonds). (The ratio of the structural units was chemically determined by N.G. Samsonova).

degree of cross-linking is directly proportional, and the amount of added sulphur in the TMTD in mixtures of like composition inversely proportional, to the content of 1,4 structure in butadiene polymers.*

TABLE 1. FORMATION OF CROSS-LINKS AND ZnDTC DURING VULCANIZATION OF NATURAL RUBBER WITH TMTD IN PRESENCE OF ZnO

Vulcanization time (min)	No. of cross-links $N_c \times 10^{-19}$ ml^{-1}	No. of ZnDTC molecules $n \times 10^{-19}$	No. of ZnDTC molecules to 1 cross-link
20	0·84	2·5	~3
30	1·66	2·9	1·7
60	3·61	5·1	1·4
110	3·27	5·3	1·6
120	4·25	5·4	1·3

In view of this we can conclude that the formation of cross-links is determined by the interaction of thiuram radicals, mainly with the hydrogen atom in the

* G. M. Sokolova participated in this part of our research.

α-position relative to the double bond of 1,4 structures. The fact that more of the sulphur from the TMTD is bound with rubbers that have a higher proportion of 1,2 structure can be explained by the addition of TMTD radicals

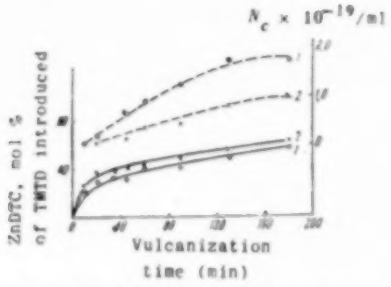
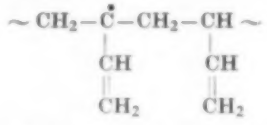


FIG. 5. Formation of cross-links (N_c) and accumulation of zinc dithiocarbamate during vulcanization of synthetic polyisoprene rubbers with a different ratio of 1,4 and 1,2 structural units. 1=polyisoprene (94 per cent of 1,4 structure), 2=polyisoprene (86 per cent of 1,2 and 3,4 structure). ——— zinc dithiocarbamate, - - - - - - - N_c. Composition of mixture (parts by weight): rubber=100, TMTD—3, ZnO=5. (Ratio of structural units determined by means of infra-red spectra in the VNIISK All-Union Scientific Research Institute for Rubber).

to the lateral vinyl groups. This process does not result in the formation of crosst links because the double bonds become saturated. Thus we deemed it important to examine the accumulation kinetics of ZnDTC in rubbers of varying structures (Fig. 5). The more rapid formation of ZnDTC in rubbers having a higher content of 1,2 structural units is rather unexpected. This points to the possible formation of dithiocarbaminic acid by the hydrogen on the tertiary carbon atom being broken off by the TMTD radical to form an active polymer radical. In this radical the lateral vinyl groups are arranged quite close together and owing to interaction between them these molecule chain segments will be insufficiently elastic. Thus it is more probable that a radical of the type



is saturated by the TMTD radical than that it participates in the cross-linking of the rubber molecule chains.

Consequently the amount of sulphur from the TMTD added to the rubber depends upon the type of the rubber and not upon the metal oxide. In the presence of the various metal oxides the saturation amount of added sulphur from the TMTD alters slightly for a given rubber (22–27 per cent for natural rubber). Furthermore, the relative amount of combined sulphur from the TMTD is almost independent of the amount of TMTD introduced or of the metal oxide.

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The metal oxide or salt obviously has a predominating influence in combining the reaction products of the TMTD with the rubber and is important for the formation of a three-dimensional structure in the vulcanizate. In this respect there is no fundamental difference between metal oxides and stearates. It follows that the crystalline structure of zinc oxide is scarcely a determinant in the production of thiuram vulcanizates for technical purposes [4]. This is corroborated by the fact that in the absence of zinc oxide we can obtain from synthetic polyisoprene rubber containing ten parts by weight of TMTD a vulcanizate with almost the same number of cross-links as a vulcanizate containing four parts by weight of TMTD and five parts by weight of zinc oxide. The vulcanizates of mixtures comprising natural rubber and ten parts by weight of TMTD in the absence of zinc oxide have satisfactory mechanical properties [2].

2. REACTION OF TMTD WITH GERANIOL AND ISOPROPYL BENZENE. THERMAL DECOMPOSITION OF TMTD

We chose geraniol as a model for the structural units of natural rubber. Isopropyl benzene (IPB) contains an active hydrogen atom on the tertiary carbon atom and is also of importance for studying the mechanism whereby vulcanizing agents operate.

The reaction with geraniol was conducted in a vaseline grease medium at 143°C and in xylene at 136°C (0·3 g TMTD, 12 ml geraniol in 100 ml of the solvent). A stream of argon (oxygen content 0·05 per cent) was passed into the flask containing the reaction mixture for 2 hr before heating. Argon was also

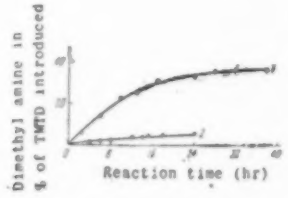

FIG. 6. Formation kinetics of dimethyl amine in reaction of TMTD with geraniol in xylene solution at 136°C. 1—0·3 g TMTD, 12 ml geraniol in 100 ml *o*-xylene; 2=0·3 g TMTD in 100 ml *o*-xylene.

bubbled in whilst the reaction was in progress and whilst the mixture was cooling after the reaction. The reaction proceeds slowly in a vaseline grease medium. On distillation of the volatile substances the same products are found as in the reaction with rubber under similar conditions. The reaction rate is considerably higher in a xylene medium (Fig. 6), moreover when TMTD is heated in it in the absence of geraniol there is an appreciable formation of amine whereas when TMTD is heated in vaseline grease no dimethyl amine is formed after 5 hr. The reaction product of TMTD with geraniol is of a bright reddish orange colour.

This same colour of the reaction mixture appears upon exposure of the mixture to ultra-violet radiation from a SVDSh-type mercury-vapour lamp in quartz ampoules at ambient temperature. This may be interpreted as indicating that the reaction proceeds via a free radical stage.

The reaction of TMTD with IPB (0·1 g of TMTD in 50 ml of IPB) was conducted under similar conditions (50 min at 136°C). The amount of unreacted TMTD (determined by conductometric titration with 0·1*N* $CuSO_4$ in the presence of hydroquinol) was 61 mol per cent of the amount introduced. In the presence of zinc oxide ZnDTC is formed ; however, owing to the poor distribution of the zinc oxide in the solution the dithiocarbamic acid is partly decomposed, as was confirmed by the formation of dimethyl amine.

Thus TMTD reacts both with rubber and with the specified low molecular compounds whose molecule contains active hydrogen to yield precisely the same products. Under these conditions it undergoes no appreciable thermal decomposition : only traces of zinc sulphide are formed in the vulcanizate but no tetramethyl thiocarbamide is found.

TMTD decomposes to form thiuram monosulphide, tetramethyl thiocarbamide, carbon disulphide and sulphur when heated in the absence of substances containing an active hydrogen atom. A weighed portion of TMTD was heated in sealed ampoules in a medium of air and argon by means of an oil bath at 143°C for $1^1/_2$–2 hr. A dark yellow liquid was formed which, after cooling, yielded light yellow crystals of tetramethyl thiuram monosulphide (TMTM) with a m. p. of 106°C.

On the addition of a Bi^{3+} ion to an aqueous extract of the contents of an ampoule after heatings the extract assumed a yellow colouration indicating the presence of tetramethyl carbamine, and on the addition of an aqueous solution of $CuSO_4$ and diethyl amine a greyish-brown precipitate was formed, indicating the presence of carbon disulphide. Consequently when TMTD decomposes under the action of heat no diethyl amine is produced. A qualitative indication of the presence of elementary sulphur in an acetone solution of the contents of an ampoule is the blue colouration at the boundary between a layer of acetone and a layer of concentrated KOH [8]. Under these same conditions TMTM decomposes to form tetramethyl carbamide and carbon disulphide.

3. DISCUSSION

The results outlined disclose that the reaction of TMTD with rubber proceeds with the participation of free radicals without their being thermally decomposed to any large extent as was pointed out in the first communications of Schele and co-workers [3]. In the absence of compounds with an active hydrogen atom TMTD thermally decomposes to give thiuram monosulphide, tetramethyl carbamide, carbon disulphide and sulphur.

Gur'ianova and Kuzina [9] showed that the isotopic exchange of TMTD with elementary sulphur operates by a radical mechanism. They consider a

radical decomposition on the C—S bond to be possible resulting in the formation of radicals (II) and (III) since for the exchange of the sulphur atom belonging to the C—S group this bond must be destroyed. It is thus extremely probable that this type of decomposition also takes place in vulcanization.

The reaction of TMTD with rubber (RH) and other substances having an active hydrogen atom appears to proceed in the accompanying manner. Radicals (I) and (II) are capable of reacting with the double bonds or of accepting hydrogen and giving unstable dithiocarbaminic acid. In all likelihood radical (III) is added to the newly forming polymer radical. Thus, is symmetrical decomposition of TMTD into radicals the reaction may proceed according to the scheme:

$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S^{*} \xrightarrow{+RH} R^{*}+[(CH_3)_2N-\underset{\underset{S}{\|}}{C}-SH] \xrightarrow{+ZnO} Zn\,DTC+H_2O$$

$$(CH_3)_2NH+CS_2$$

$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-SH\cdot HN(CH_3)_2$$

In asymmetrical decomposition the reaction proceeds according to the scheme:

$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S-S^{*} \xrightarrow{+RN} RS^{*}+[(CH_3)_3N-\underset{\underset{S}{\|}}{C}-SH],$$

and continues as in the preceding scheme.

The radicals R* and RS** may either be combined together and with the rubber molecule to form cross-links in the vulcanizate or become saturated with radicals (I) or (III). The presence of specific amounts of added sulphur from the TMTD (22–25 per cent of the amount introduced in the form of TMTD in the case of natural and synthetic polyisoprene rubbers) and of decomposing dithiocarbamic acid or of ZnDTC in the course of formation (66 per cent) is apparently accounted for by the presence of a given ratio of symmetrical and asymmetrical dissociation of the TMTD into radicals.

According to the above scheme the thiuram vulcanizate must contain mainly C—C and C—S—S bonds and an insignificant number of C—S—S—C bonds: this is consistent with the results obtained by Dogadkin and Tarasov on the relaxation kinetics and with the isotopic exchange of thiuram vulcanizates with elementary rubber [10].

When no substances containing an active hydrogen atom are present in the system, the TMTD radicals that are formed upon heating are subjected to further, more intense decomposition. In the light of the decomposition products we identified this process can be described in the subjoined manner:

$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-S^{\bullet} \longrightarrow (CH_3)_2N-\overset{\overset{S}{\|}}{C}-S^{\bullet} + {}^{\bullet}S^{\bullet} \xrightarrow{+(CH_3)_2N-\overset{\overset{S}{\|}}{C}^{\bullet}} \longrightarrow (CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 + \text{elementary sulphur};$$

$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S^{\bullet} \longrightarrow (CH_3)_2N^{\bullet} + CS_2 \xrightarrow{+(CH_3)_2N-\overset{\overset{S}{\|}}{C}^{\bullet}} (CH_3)_2N-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 + CS_2$$

The reaction of TMTD with rubber is accompanied by the formation of chemically and thermally stable cross-links between the molecular chains of the rubber. Were only a bimolecular reaction to take place between the TMTD and the rubber an addition product of TMTD and rubber would be formed plus dithiocarbamic acid, but cross-links would not arise. Stable C—C bonds are formed clearly as a consequence of radical reactions. Direct confirmation that the reaction proceeds by a radical mechanism is furnished by the results that emerged from a study of the electronic paramagnetic resonance spectra of mixtures comprising natural rubber and TMTD heated in an argon atmosphere under a vacuum at 140 and 180°C (Fig. 7).*

The spectrum has four peaks which gradually disappear on cooling but reappear on subsequent heating. On heating at 180°C for 50 min the peaks abruptly fall, i.e. the reaction of the TMTD with the rubber terminates.

The thermal decomposition of the TMTD radicals in the presence of rubber or other substances containing an active hydrogen atom is less economical energetically than an attack by the TMTD radicals on the hydrogen atom or their reaction with the double bonds. This is corroborated by the accumulation in the system of other products in the presence of such substances. As has previously been observed tetramethyl thiocarbamine, a characteristic thermal decomposition product of TMTD, was not found by us in the reaction of TMTD with rubber, geraniol, and isopropyl benzene.

The behaviour of TMTD undre vulcanization conditions recalls the action of peroxides and TMTD in the polymerization process [11]. The maximum noted earlier on the kinetic curve for the addition of sulphur from TMTD (which distinguishes this process from other cases of polymerization) can obviously be accounted for by some of the thiuram groups being added to the rubber in the

* We conducted these tests in S. E. Bresler's laboratory at the Institute of High Molecular Compounds, USSR Academy of Sciences, assisted by E. M. Saminskii and E. N. Kazbekov. A more detailed analysis of these spectra will appear in a later communication.

initial stages and being split off in a subsequent stage as carbon disulphide or as a dithiocarbamyl radical. A process of this nature is more likely for the radical

$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S-S\,.$$

This is confirmed by the findings on the addition of sulphur from TMTD to rubber on heating when there is no maximum on the kinetic curves.

FIG. 7. Electron paramagnetic resonance spectrum of a mixture of natural rubber (NR) (100 parts by weight) and TMTD (3 parts by weight) 10 min after heating briefly at 140°C.

In the vulcanization of rubber with thiuram disulphide the metal oxides are mainly operative in combining the dithiocarbamic acid. As we showed earlier (1) the products of its decomposition (carbon disulphide and dimethyl amine) accelerate the thermal oxidative decomposition of the vulcanization lattice. Thus, if the acid is not combined as a stable zinc salt under the conditions of vulcanization, reversion of vulcanization occurs as a distinct phenomenon.

We extend our grateful thanks to S. E. Bresler, E. M. Saminskii and E. N. Kazbekov for studying the para-magnetic resonance spectra of mixtures with thiuram.

CONCLUSIONS

(1) When rubber is vulcanized with tetramethyl thiuram disulphide, sulphur and nitrogen from the thiuram are added to the rubber in the form of radicals. Furthermore, a clearly defined maximum occurs on the kinetic curve for the addition of sulphur in the initial vulcanization period.

(2) The presence of a maximum on the kinetic curves for the addition to the rubber of sulphur from the thiuram is explained by the decomposition of the sulphur-containing radicals that have been added to the rubber and the subsequent formation of carbon disulphide.

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(3) The unequal relative amounts of sulphur and nitrogen from the thiuram that are added to the rubber entitle us to conclude that under vulcanization conditions symmetrical and asymmetrical decomposition of the thiuram into radicals take place.

$$(CH_3)_2N-\underset{\underset{S}{\|}}{C}-S\cdot\ ;\quad (CH_3)_2N-\underset{\underset{S}{\|}}{C}-S-S\cdot\ ;\quad (CH_3)_2N\underset{\underset{S}{\|}}{C}\cdot$$

(4) These radicals interact with the rubber to form macroradicals which react with each other and with the rubber molecules to produce a three-dimensional vulcanizate lattice.

(5) The dithiocarbamyl radicals accept hydrogen from the α-methylene groups of the rubber molecules to form dithiocarbamic acid, which, in the presence of zinc oxide, is combined into stable zinc dithiocarbamate. Here a fine space lattice emerges and reversion of vulcanization does not take place.

(6) In mixtures without metal oxides and in mixtures containing magnesium and calcium oxides the dithiocarbamic acid produced dissociates into dimethyl amine and carbon disulphide. Here reversion of vulcanization comes about owing to acceleration by these substances of the thermal oxidizing decomposition of the vulcanization lattice.

(7) In mixtures of natural rubber containing lead and nickelous oxides the space lattice is not formed and, furthermore, neither is carbon disulphide or dimethyl amine. The metal dithiocarbamates obtained here are apparently combined with the rubber.

(8) The concentration of cross-links in a vulcanizate rises in direct proportion to the number of 1,4-type structural units in the rubber, but the amount of added sulphur and the rate of accumulation of zinc dithiocarbamate are inversely proportional.

(9) When thiuram interacts with geraniol and isopropyl benzene, as with rubber, dithiocarbamic acid is yielded which dissociates into dimethyl amine and carbon disulphide.

(10) On heating thiuram in the absence of substances containing active hydrogen in their molecule it decomposes to give tetramethyl thiuram monosulphide, carbon disulphide, tetramethyl thiocarbamine and sulphur.

Translated by G. CAMERON

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EMULSION POLYMERIZATION UNDER THE INFLUENCE OF γ-RADIATION*

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(*Received* 13 *December* 1958)

A LARGE number of papers have recently appeared devoted to the study of polymerization under the influence of nuclear radiation [1]. All these studies were conducted under conditions of bulk polymerization or in solutions of the monomers. One single paper reports on emulsion polymerization involving radiation [2]. The use of radiation to initiate emulsion polymerization enables certain features of this form of polymer preparation to be accounted for and in addition it has a practical bearing.

The present paper relates to a study of the polymerization of styrene and methyl methacrylate in emulsions stabilized with the following emulsifiers: sodium laurate, MK (a mixture of sodium salts of sulpho acids of the fatty series with the mean composition $C_{15}H_{31}SO_3Na$), Nekal† (a sodium salt of dibutyl naphthalene sulpho acid) and cetyl pyridine bromide. For purposes of comparison the same monomers were polymerized in bulk. The exposures were done in an apparatus designed at the L. Ia. Karpov Institute of Physical Chemistry [3]. The source of the γ-radiation was ^{60}Co (400 g equiv. of radium). The experiments were carried out in the dilatometer illustrated in Fig. 1 and the rate of polymerization was determined from the reduction in volume of the system. The emulsion was stirred by the magnetic agitator and temperature control was ensured by feeding into the jacket water from an "ultrathermostat".

The monomer in the emulsifier solution was freed from dissolved air by freezing and defreezing under a vacuum and transferred to the dilatometer, which was fixed to the apparatus, without coming into contact with air. Polymerization was conducted at a 1 : 3 ratio of the hydrocarbon and aqueous phases (by weight) and with an emulsifier concentration of 3 per cent (referred to the water) throughout the temperature range 25–87°C. The absorbed energy was determined in the same dilatometers by the oxidation of Mohr's salt in a 0·8 *N*

* Vysokomol. soedin. **1**: No. 1, 68–71, 1959.

† *Translator's note.* A detergent.

solution of sulphuric acid saturated with air. The exposure intensity amounted to 4×10^{18} eV/l. sec. The resulting latex was coagulated and the polymer re-precipitated from toluene with methyl alcohol.

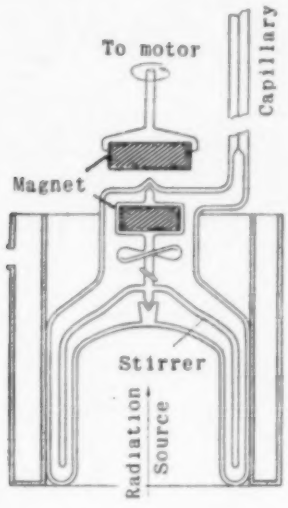

FIG. 1. Dilatometer.

The mean molecule chain length (P) was computed from the results of viscometric measurements: for polystyrene (in toluene) [4] $[\eta]=1{\cdot}23\times10^{-4}\,(104\,P_1)^{0{\cdot}72}$. Since this equation is derived for fractionated polymers, the values listed in the Tables for the mean degree of polymerization (P) of non-fractionated polymers were worked out from relationship [5]:

$$\frac{P}{P_1}=2\left[\frac{2}{(a+2)\,(a+1)\Gamma\,(a+1)}\right]^{1/a}=0{\cdot}765 \text{ where } a=0{\cdot}72\,.$$

For non-fractionated methyl methacrylate (in chloroform) [6]:

$$[\eta]=2{\cdot}52\times10^{-3}\;P^{0{\cdot}80}\,.$$

The emulsion polymerization of styrene proceeds at a constant rate up to a conversion of 50–60 per cent (Fig. 2). The initial rate of the reaction in emulsion is higher than in bulk by 100–300 orders (*cf.* Table 1). The emulsifiers can be classified as follows according to their influence on the over-all polymerization rate: lauric acid sodium salt (0·8 g of polymer to 100 ml of soap solution per sec), emulsifier MK (0·6), Nekal and cetyl pyridine bromide (0·2). For emulsion polymers P is about ten orders larger than for bulk polymers. The emulsion polymerization rate throughout the temperature range 25–87°C, and the mean mol. wt. of the polymers formed are almost indentical.

TABLE 1. STYRENE POLYMERIZATION UNDER ACTION OF γ-RADIATION
(Intensity 4×10^{18} eV/l. sec)

Polymerization conditions	Temp. °C	Monomer conc., (C), mol/l.	Initial polym. rate $V \times 10^5$, mol/l. sec		Overall activation energy E_o kcal/mol.	$[\eta]$ 1000 ml / g	Mean polymer chain; length $P \times 10^{-4}$	$Vin = \frac{V}{P}$	$\frac{K_p}{\frac{1}{2}}$ / K_{ter}	K_{ter}
In bulk	25	8·66	0·88		4·8±0·3	—				
	40	8·56	1·35			0·8	0·14	10^{-8}	1×10^{-2}	7×10^6
	70	8·29	2·54			1·0	0·20			
In emulsion, emulsifier MK (3% referred to water); ratio of phases "monomer : water" = 1 : 3	25	0·57*	0·8†	2·2‡		4·5	1·65			
	50	0·57	1·0	2·6		4·6	1·73			
	70	0·57	1·0	2·6	1±1	4·4	1·57	10^{-6}		
	87	0·57	1·0	2·6		4·3	1·50			
In emulsion, emulsifier sodium laurate (3%); ratio of phases "monomer : water" = 1 : 3	50	1·24	1·6	4·1	0	4·0	1·47			
	70	1·24	1·7	4·2	0	4·0	1·47	10^{-6}		
	87	1·24	1·2	2·8		4·2	1·0			

Significance of symbols *, †, ‡ etc. as follows: *, monomer concentration in colloidal ions *(c)* mole/l.; †, initial polymerization rate $V_1 \times 10^5$ g polymer in 100 ml soap solution per sec; ‡, initial polymerization rate $V_1 \times 100$ mole in l. (soap + styrene) per sec.

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The time-dependence of the reaction with different emulsifiers was studied after the radiation source had been switched off. This was done after 15–50 per cent conversions had been achieved. Figure 2 shows that after radiation is discon-

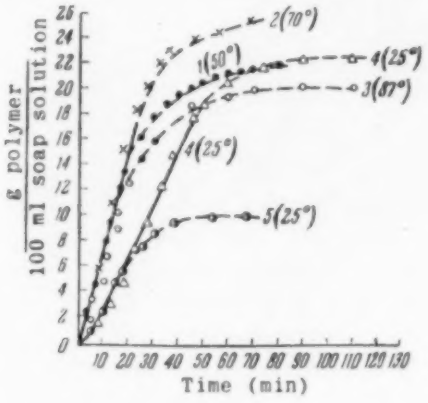

FIG. 2. Emulsion polymerization of styrene. Curves 1–3: emulsifier = sodium laurate; curves 4 and 5: emulsifier MK; ——— radiation; - - - - - - - polymerization without radiation.

tinued a considerable amount of polymer forms (15–20 per cent of the original monomer amount); polymerization continues for 60–65 min after the source has been switched off.

TABLE 2. BULK AND EMULSION POLYMERIZATION OF METHYL METHACRYLATE UNDER THE ACTION OF λ-RADIATION

(Emulsifier MK = 3% (referred to water), ratio of phases "monomer : water" = 1 : 3, intensity 4×10^{18} eV/l. sec)

Conditions of polymerization	Temperature °C	Over-all polymerization time, min	Polymer yield %	Initial polymerization rate, %/min	$\frac{[\eta]}{100 \text{ ml}/\text{g}}$	$P \times 10^3$
In bulk	25	125	12·2	0·11	—	—
	50	80	10·3	0·15	1·35	2·63
	70	68	10·5	0·18	—	—
In emulsion	25	12	72·0	13·8	—	—
	50	12	73·0	13·8	5·0	13·2

The polymerization rate of methyl methacrylate in emulsion is also 100–200 orders higher than of polymerization in bulk and P is greater by five orders (*cf.* Table 2), reaching 73 per cent at room temperature in 12 min.

These results signify that in emulsion polymerization under the action of γ-radiation approximately the same increase in the reaction rate and in P (relative to bulk polymerization) arises as in the presence of peroxides and azo-compounds.

The characteristic features of emulsion polymerization under the influence of γ-radiation are:

1. Temperature independence of the over-all rate (E_o does not exceed 1 kcal/mol.).

2. Formation of appreciable quantities of polymer after discontinuation of exposure.

It has been demonstrated [7] that in the emulsion polymerization of styrene under the action of initiator substances E_o lies between 10–17 kcal/mol, which is 4–11 kcal less than with polymerization in homogeneous system. This is determined by a reduction in the activation energy of the chain initiation reaction (E_{in}) and an increase in the activation energy of the chain termination reaction (E_{ter}) under the conditions of emulsion polymerization.

In the advanced stages of styrene photopolymerization in bulk a decrease in E_o of 2–4 kcal relative to the initial stage also occurs [8]. With a 40 per cent polymer concentration in the monomer, equivalent to its concentration in the polymer-monomer particles in the emulsion polymerization of styrene [9], E_o decreases by 2 kcal entirely as a result of the increase in E_{ter}. In the advanced stages of polymerization E_{ter} appears to be governed by the activation energy associated with the reciprocal diffusion of the polymer radicals in the viscous medium. The literature contains no information on the activation energy of diffusion, E_{diff}, of polymers in a viscous medium but the activation energy of a viscous flow of polystyrene in concentrated solutions (40–60 per cent) is close to E_{diff} and lies in the range 6–12 kcal/mol [10]. The energy associated with the diffusion of low molecular compounds into solid polymers is 9–12 kcal/mol.

Since under the influence of γ-radiation $E_{in}=0$ and for styrene $E_p \sim 6$ kcal/mol, then in emulsion polymerization, if we assume that termination occurs by the interaction of two polymer radicals, $E_{ter} \sim 12$ kcal/mol which seems to correspond to E_{diff} in concentrated polymer solutions.

Just as in the advanced stages of bulk polymerization K_{ter} is markedly lower with polymerization in an emulsion than with polymerization in low viscosity media. Thus for the bulk polymerization of styrene K_{ter} at 40 per cent conversion is 10^3 orders smaller than K_{ter} at the start of the reaction [8]. Table 1 shows that the ratio $K_p/K_{ter}^{1/2}$, worked out from the initial bulk polymerization rate and from P, amounts to 1×10^{-2} and $K_{ter}=7\times10^6$ at 40°C (the propagation constant (K_p) is assumed [11] to be $1{\cdot}44\times10^6\times e^{-6300/RT}$) in agreement with the literature [11 and 12].*

* Table 1 shows that E for the polymerization of styrene in bulk under the action of γ-radiation is close to the reported values of $E_p-{}^1/_2E_{ter}$ for this monomer [11].

Calculated from the reaction rate and P the value of K_{ter} in emulsion polymerization under our experimental conditions ranges from 10^1–10^3.

The low chain termination reaction rate and, correspondingly, the long life of the polymer radicals in emulsion polymerization seems to be the cause behind the polymerization that takes place after discontinuation of exposure. It is also possible that this polymerization stems from hydrogen peroxide formed by radiolysis of the water.

The rate of polymerization in emulsion under the action of radiation, as opposed to polymerization in bulk, also accelerates owing to the increase in the initiation rate. This is determined by the fact that in bulk polymerization the initiating radicals are formed from monomer molecules whereas with polymerization in an aqueous emulsion these radicals are formed by radiolysis of the water (H and OH radicals) and possibly of the emulsifier molecules too. Table 1 shows that the initiation rate of the bulk polymerization of styrene is of the order of 10^{-8}, and of its emulsion polymerization, 10^{-6}. As regards emulsion polymerization 5×10^{19} eV are expended in producing 1g of polystyrene and for each 100 eV of absorbed energy 10^4 monomer molecules react, while for bulk polymerization these figures are respectively 5×10^{21} eV and 10^2 molecules.

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CONCLUSIONS

The authors show that the following characteristics emerge in the polymerization of styrene in emulsions, stabilized with soap, under the action of γ-radiation.

(1) Temperature independence of the over-all polymerization rate;

(2) The formation of substantial amounts of polymer after the radiation source has been switched off.

Possible causes of these phenomena are considered.

Translated by G. CAMERON

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SYNTHESIS AND MECHANICAL PROPERTIES OF ISOTACTIC POLYSTYRENE*

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(*Received* 12 *July* 1958)

IN recent years, thanks to the discovery of new methods for carrying out polymerisation (catalytic stereospecific polymerization) it has become possible to synthesize anumber of polymers, possessing a regular chain structure [1–3].

The property of easy crystallization and a number of properties bound up with this sharply distinguish these polymers from polymers obtained from the same monomers by the usual reactions of radical polymerization. Besides this, the process of stereospecific synthesis presents great theoretical interest in as much as it represents the first example of the polymerization synthesis of macromolecules of previously fixed structure, carried out under laboratory conditions without the aid of enzymes. These two circumstances explain the great interest in the production and properties of regular polymers.

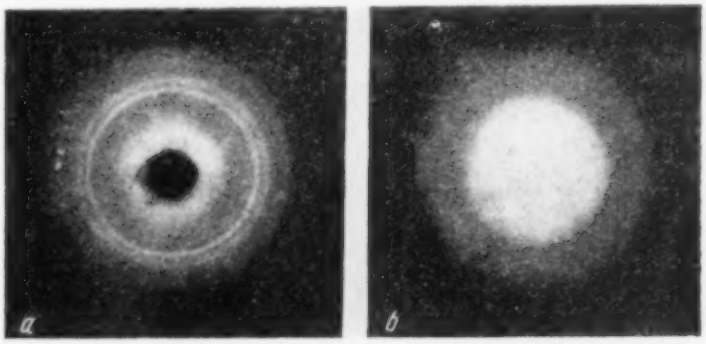

FIG. 1. (a) X-ray diagram of isotactic crystalline polystyrene (b) X-ray diagram of amorphous polystyrene.

The aim of present work was to obtain and investigate the mechanical properties of isotactic polystyrene not already described in the literature. This ma-

* Vysokomol. soedin. 1: No. 1, 94–102, 1959.

terial is also of especial interest because it presents an example of a crystalline plastic, the vitrification region of which lies higher than room temperature. Crystalline polymers with high temperatures of vitrification and fusion, are lately finding increasing application in practice. The region of the usual temperatures for the treatment of these polymers not only lies lower than the temperature of fusion but lower also than the vitrification temperature, and this distinguishes them from those polymers, such as polyethylene, Capron, Nylon, Guttapercha, and several others whose vitrification temperature is lower than room temperature, and which, as a rule, are used in the range between the temperatures of fusion and vitrification. This circumstance unavoidably brings about a difference in the processing properties of the first and secone group of materials.

For the synthesis of isotactic polystyrene we used two catalytic combinations, know as Ziegler type catalysts: $TiCl_4+Al(C_2H_5)_3$ and $TiCl_3+Al(C_2H_5)_3$.

Purification of the monomer was performed as follows. Technical styrene was washed with a 10% solution of soda, and then with distilled water, to give a neutral reaction, dried over fused calcium chloride, and distilled under reduced pressure (40 mm). Before polymerization the dissolved gases were removed from it by repeated freezing in a high vacuum. The titanium tetrachloride was distilled over copper filings at 133° before introduction into the reaction. The titanium trichloride was obtained by reduction of titanium tetrachloride with metallic antimony [4]. The solution of triethyl aluminium of the necessary concentration was prepared by dilution of its 80% solution in "rubber" benzine, with *n*-heptane.

The polymerization was performed in a flask with reflex condenser, equipped with a stirrer, dropping funnel and a burette for letting in the required quantity of triethyl aluminium solution. The construction of the equipment allowed the filling of the burette and of the dropping funnel, and the mixing of the constituents in an atmosphere of inert gas, the argon or nitrogen used being first thoroughly dried and purified.

In using the catalytic mixture a number of ratios for $TiCl_4$: $Al(C_2H_5)_3$ were used (1 : 0·13, 1 : 0·66, 1 : 1, 1 : 8, and 1 : 10). In all cases the weight of $TiCl_4$ was around 1 per cent of the weight of styrene while the quantity of $Al(C_2H_5)_3$ introduced into the reaction as a 10 % solution, was varied.

It was found that with an excess of titanium tetrachloride in the catalytic mixture the polymerisation took at a high rate even at room temperature but the polysterene obtained contained practically no isotactic fraction. Isotactic polymer is formed in the system only with an excess of triethyl aluminium. In this case polymerization proceeds at a noticeable rate only with increased temperature. In our experiments the temperature was varied from 90–100°. The yield of isotactic polymer compared with the total amount of polymer did not exceed 30 per cent. Apparently, with an excess of titanium tetrachloride the rapid polymerization as initiated dy the titanium tetrachloride itself and proceeds in the solution according to the well known cationic mechanism which does not secure specific control. With an excess of triethyl aluminium a considerable part of the titanium

tetrachloride is reduced by the triethyl aluminium to compounds of lower valency, which in combination with the triethyl aluminium give a stereospecific catalytic complex.

Considerable yields of isotactic polystyrene were obtained using the catalytic combination $TiCl_3$ and $Al(C_2H_5)_3$, which possessed high stereospecificity [5]. In this case the content of the isotactic fraction reached 95 per cent. In our experiments the quantity of $TiCl_3$ was in all cases 1 per cent of the weight of monomer. We used ratios of $TiCl_3$: $Al(C_2H_5)_3$ of 1 : 0·1, 1 : 0·3, 1 : 1 ; 1 : 5 and 1 : 10. The reaction was carried out at 100° over 30 hr. The ratio of the components has practically no effect on the yield of isotactic product but an excess of $Al(C_2H_5)_3$ is useful as a prophylactic water removing material. These results agree with the data of Natta for polymerization of propylene [17].

When the reaction had ceased the polymer was washed with methyl alcohol. The atactic fraction was separated from the isotactic by extraction with methyl ethyl ketone in which atactic polystyrene is soluble but not the isotactic [6]. Isotactic polystyrene, separated in this way from the reaction mixture had a crystalline structure, established by X-ray photographs. The X-ray pictures of the crystalline isotactic, and the amorphous atactic polystyrene are shown in Fig. 1a and 1b.

Crystalline isotactic polystyrene is practically insoluble in the cold in any of the solvents we tried (benzene, toluene, xylene, methyl ethyl ketone etc). However on heating in boiling benzene, toluene and xylene it is almost completely soluble. The insoluble part as a rule is about 3–5 per cent of the polymer used, and consists apparently of the highest molecular weight portion of the isotactic polymer with admixture of inorganic remains of the catalyst. The solutions obtained are quite stable when cooled to room temperature and can be used for viscosimetric determinations.

For complete solution the crystalline isotactic polystyrene must be made amorphous. For this we subjected it to heating in evacuated ampoules at 300°, i.e. above the fusion temperature (the fusion temperature of crystalline polystyrene is about 230°), and then to rapid cooling. In this way the polystyrene cannot crystalline and solidifies in the form of a glass.

Solution of the amorphous isotactic polystyrene in the corresponding solvents (benzene, toluene), occurs considerably easier. On addition of methyl alcohol to the benzene or toluene solution a precipitate of polymer is formed. If the precipitation is carried out in the cold, the precipitate has an amorphous structure. Its X-ray diagram is analogous to that of ordinary atactic polystyrene. If carried out from hot solutions then the precipitated polymer can partially crystallize. Repeated crystallization of the amorphous polymer can be carried out by heating it in boiling *n*-octane or *n*-heptane or other non-solvent suitable for crystallization. The density of the isotactic crystalline polystyrene, determined by the gradient tubes method [7] was 1·08 g/cm³. The density of the amorphous isotactic polystyrene was 1·05 g/cm³ i.e. the same as the density of ordinary atactic polystyrene

The crystalline and amorphous isotactic polystyrene were subjected to thermo-mechanical tests on a dynamometric balance. The samples were prepared in the form of little tablets of diameter 10 mm and thickness 3 mm by compression in a laboratory press. In Fig. 2 are shown the results of these thermo-mechanical tests.

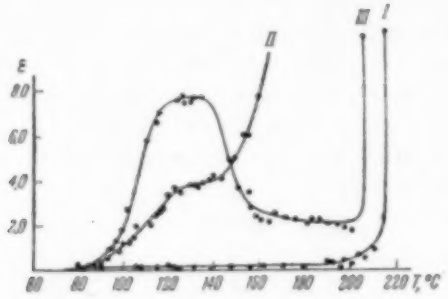

FIG. 2. Thermomechanical curves for polystyrene, I—Crystalline isotactic polystyrene, II—amorphous isotactic polystyrene, III—atactic polystyrene.

On the abscissa is the temperature and on the ordinate the difference in the degree of deformation of the tablets under the action of loads of 240 and 10 g related to the original thickness of the tablets. The thermomechanical curve I for crystallized isotactic polymer shows that within a wide range of temperature, in contrast with ordinary atactic polystyrene (curve II), the sample remains practically underformed in the conditions of the experiment and only at temperatures of the order of 220° does it flow and become a viscofluid. Amorphized isotactic polystyrene (curve II) at temperatures of the order of 80°, like the atactic, reaches a highly-elastic condition but on raising the temperature further consolidation of the sample sets in, its deformability drops and flow begins only on fusion of the crystals.

It was established by X-ray diagram that the consolidation of the sample is governed by its crystallization, which begins above the temperature of vitrification of the amorphous polymer. In other words, increased heat stability returns to the isotactic polystyrene samples, made amorphous by fusion and quick cooling, as a result of its being heated above the temperature of vitrification. The possibility of crystallization of the isotactic polystyrene is conditioned by the regular structure of its chains, made up of links joined "head to tail" and the distribution of the phenyl side groups in relation to the main chain is such that over considerable areas of the chain one and the same spacial configuration of tertiary assymetric carbon atoms is repeated (left or right) [8].

This regularity of the chain arising in the process of polymerization does not dissappear on fusion of the polymer crystals, for in order for this to take place it is necessary to break each of the little chains in many places and re-join the chain breaks so formed in a random way. On fusion this does not occur. The

chains, on fusion, preserve the correct sequence of assymetric atoms although they change their form. Therefore the polymer made amorphous by fusion and quick cooling, during which crystallization cannot take place, preserves its capability of repeated crystallization. However, the recrystallization, as with all crystallizable polymers, can take place only above the vitrification temperature when mobility of the links is sufficiently high.

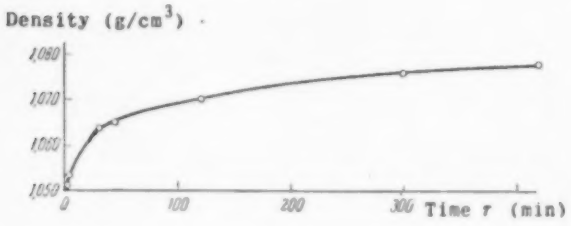

FIG. 3. Change of density (d) of amorphized isotactic polystyrene with time of heating.

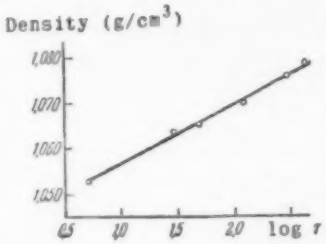

FIG. 4. Change of density of amorphized isotactic polystyrene with logarithm of time of heating at 100°C.

For assessing the speed of recrystallization we measured the density of the amorphous isotactic polystyrene samples for various times of heating above the vitrification temperature (at 100°). The increase in density of the sample with time of heating, which is related to the increase in the degree of crystallization, is shown in Fig. 3. The curve obtained becomes straight when plotted with logarithmic axes (Fig. 4). A similar relationship is found on studying the rate of recrystallization of fused and quickly cooled polyethylene of low stress [9].

With the aid of the dynamometer, described in the work of one of us and Sogolova [11] we studied the behaviour of a film of isotactic polystyrene on extension, over a wide range of temperature. The films were produced from 4% benzene solutions of isotactic polymer on cellophane supports by slow evaporation of the solvent. The results of the experiments are shown in Fig. 5, where on the abscissa is shown the relative deformation in per cent, and on the ordinate the amount of strain related to the original of the sample (σ).

A characteristic effect was that below the vitrification temperature unoriented films of isotactic polymer appear as completely fragile. From Fig. 5 it can be seen that right up to a temperature of 80° the samples suffer tearing even in the region of small Hookian deformations. Reasonable extension is only seen in the region of vitrification and above. This effect is found in some degree or other in all the unoriented crystalline polymers, deformed below the vitrification temperature. The usual notions on the stability of crystalline polymers, connected with the high deformability, are justified only in the case where the material is used above its vitrification temperature.

The last stipulation is automatically fulfilled at room temperature for example with products from polyethylene Capron, Nylon, and several other crystalline plastics. On cooling to the vitrification temperature and below these polymers, as also isotactic polystyrene, lose deformability and become fragile. This is be-

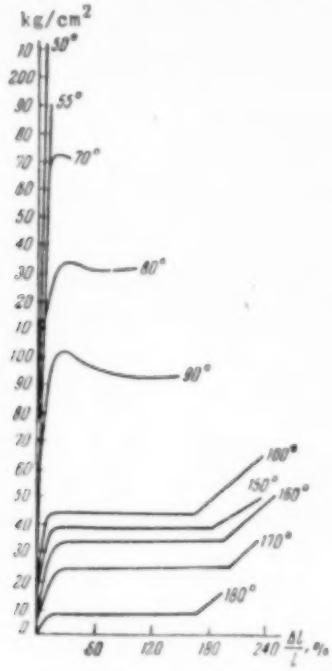

FIG. 5. Extension curves of films of isotactic polystyrene (against each curve is shown the temperature at which extension was carried out).

cause for extension of the crystalline polymer below the vitrification temperature one must consume energy in breaking the crystals, oriented "unsuccessfully" in relation to the direction of the acting mechanical field and also energy in reorganization of the amorphous structure. For this considerable external force is required which increases the stability of the crystalline sample.

The resulting elastic deformations, characteristic of amorphous polymers in the vitreous state, can arise from the action of relatively small forces, since they are connected only with the consumption of energy on the reorganization of the amorphous structure. It is known that the increase in the elastic properties of amorphous polymer glasses is connected with their relatively loose packing of the solid macromolecules. This source of elasticity is absent in crystalline polymers for these are packed quite densely. Finally, it is known that on crystallization in isotropic polymer materials secondary crystal formations arise — spherulites. It was shown recently that the formation of spherulites is accompanied by the

growth of radial micro-cracks in the sample [10]. These cracks may be the source of fragility of crystalline polymer materials deformed below the vitrification temperature since the closing up of the cracks is impossible in these conditions because of the low mobility of the chains. Altogether all these circumstances bring about the lowering of the mechanical properties of unoriented crystalline polymers in the region below the vitrification temperature. For instance polyethylene terephthalate which finds wide usage in the form of oriented fibres and films, being crystalline in the unoriented condition, is very fragile at room temperature and is only a little deformable material (temperature of vitrification of polyethylene terephthalate is 90°).

In the region of the vitrification temperature and at higher temperatures the energy of thermal motion is sufficient for reorganizing the amorphous structure. Non-crystalline polymers at there temperatures, are transformed into easily deformed rubber-like materials. Extension of a crystalline polymer above the vitrification temperature, takes place via the amorphous stage and is accompanied by recrystallization of the sample [11, 13] i.e. to bring it about introduction of external energy must be made, sufficient to bring about the mechanical "fusion" of the crystals in the micro-regions. However, the molecular regroupings in each of the amorphous micro-regions, determining the development of deformation and preceding recrystallization in this region, occur easily, and do not demand the consumption of additional external energy, as is the case with deformation of polymer below the vitrification temperature. This also facilitates the closing of the cracks and consequently lowers the fragility and raises the stability of the sample.

It can be seen from Fig. 5 that at 80° and above, deformation of films of isotactic polystyrene is increased. On the extension curves three regions are seen characteristic for crystalline polymers [11]. The horizontal regions correspond to the appearance and development of "necks" i.e. to the transformation of the sample into the oriented state.

Orientation is accompanied by destruction of the spherulites and the appearance of anisotropy of properties. The materials then becomes considerably less fragile at room temperature. To obtain good orientation of the crystals in the polymer the extension must be carried out at as low a temperature and as quickly as possible since if this is not done, under the influence of thermal motion a part of the chains will be able, during the extension, to escape from the influence of the mechanical field and form isotropically distributed crystals [13].

We were convinced that the extensions of the isotactic polystyrene samples observed in our experiments were not connected with their poly-dispersion and molecular weight, since the character of the extension curves and break-extensions for films obtained from fractions with weights 350,000 and 750,000, are practically indistinguishable from those for films from unfractionated polymer. For the fractionation we used solutions of isotactic polystyrene in toluene. Precipitation was performed with methyl alcohol.

The molecular weight of the fractions was determined by viscometry in toluene solutions and calculated from the formula $[\eta] = 1{\cdot}10 \times 10^{-4} M^{0{\cdot}725}$, obtained in work [15].

The heights of the horizontal parts of the extension curves, which can be interpreted as the stress of recrystallization (σ_p), become lower with increasing temperature. However in the region of temperature corresponding to higher rates of crystallization, this fall becomes slower which corresponds to the appearance of "blunt-portions" on the graph of dependence of crystallization stress on temperature (Fig. 6). This apparently is connected with the kinetics of the process of breaking the crystals and recrystallization during the development of deformation. The magnitude of the recrystallization stress depends on the temperature and the number of crystals formed in unit volume. With increasing temperature the energy of thermal motion of the micromolecules increases which brings

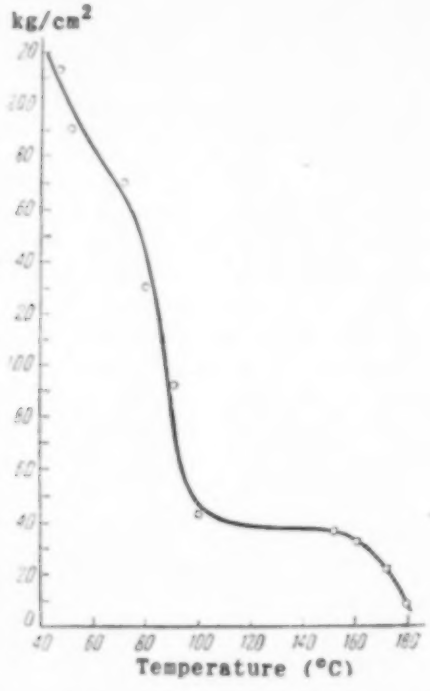

FIG. 6. Dependence of stress of recrystallization (σ_p) on the temperature of extension.

about a decrease in σ_p ; but a rise in temperature leads also to an increase in the number of crystals formed in unit time in unit volume on recrystallization and this in its turn, brings in an increase in the stress necessary to destroy the crystalline structure of the sample. These two factors in a given temperature

region can compensate each other and this shows up on the corresponding extension curves. Similar effects are observed on extension of films of crystalline polyethylene terephthalate [13] and a few other polyesters of polyamides [14].

The effect of temperature at elongation of crystalline films of isotactic polystyrene on the character of their subsequent shrinkage was studied. For this films of crystalline isotactic polystyrene were elongated on a Polanyi dynamometer to 100 per cent at the same rate for various temperatures, all above the vitrification temperature of the polystyrene. After obtaining the said elongation the extension was stopped and the dynamometer oven removed. The rapid cooling of the sample to room temperature so obtained permitted the fixing of its deformation at the moment of stopping the extension (of course with exclusion of the Hookian component of deformation, which disappeared at practically the same for as removal of the stress). The films extended in this way were hung up freely in a thermostat and with the aid of a cathetometer their shrinkage was measured at gradually increasing temperature. The rate of temperature rise was 0·3°C/min. The curves

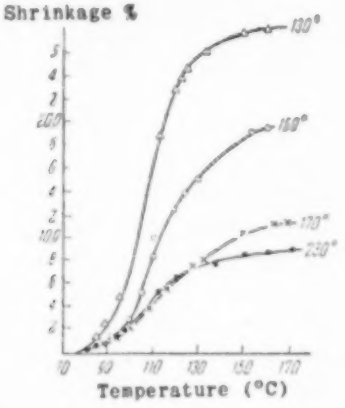

FIG. 7. Nature of shrinkage of oriented film of isotactic polystyrene on heating (against each curve is shown the temperature at which the orientation was carried out).

in Fig. 7 show the shortening of the extended films with increasing temperature. It can be seen that, independently of the temperature of the preliminary extension, (these temperatures are shown against each curve), the shrinkage of the crystalline films always begins at the vitrification temperature of the polystyrene (80°) which is practically independent of the temperature of crystallization of the sample during deformation. The crystalline polymer always "remembers" its temperature of vitrification. Also the limiting value of shrinkage characterizing the non-equilibrium length of deformation is less the higher the extension temperature. This is connected with the relaxational character of the process of deformation of crystalline polymer.

It has been shown above that to obtain good orientation, giving an improvement in the mechanical properties of the film, the temperature at which the extension takes place must be as low as possible and the rate of extensions as high as possible. However, these factors, from what was just said, will lead to an increase in the subsequent shrinkage of the film on heating it, during working, above the vitrification temperature. A compromise solution apparently can be found, if the film, orientated at as low a temperature as possible is heated afterwards in the extended state above the vitrification temperature. The crystals, formed additionally on the subsequent heating, are oriented in relation to the acting mechanical field, since during the heating process there does not take place a continuous mechanical disruption of the structure, and the nearby order, in the oriented amorphous regions is prepared for the appearance of crystals with parallel orientation of the crystallographical axes.

The kinetic maxima observed on the extension curves (see Fig. 5) in the region of not too high temperatures, remind one of the corresponding maxima on the extension curves of amorphous polymer glasses in the region of constrained elasticity [12], which also points to the common relaxational character of the deformation processes in crystalline polymers and amorphous polymer glasses. Such a mechanism can easily be imagined as a basis for the ideas on the bundle structure of polymers [16].

According to this idea the polymer is constructed of formations, consisting of long bunches or bundles of parallel oriented chains. These bundles are analogous to the "clusters" in low molecular liquids, but owing to the long times of relaxation, each polymer bundle exists for an incomparibly longer time than the liquid cluster. Under the influence of thermal motion, on account of the flexibility of the polymer chains the bundle can bend and reorganize itself. The molecular regrouping process can lead to a variation of the thickness of the bundle within wide limits, to the destruction of some bundles and formation of others. The bundle can be longer than any individual chain ; a long bundle can be constructed from comparatively short polymer molecules, in a similar way to that in which a thread can be constructed from a number of short filaments. Hence the length of the bundle during molecular regrouping can also vary within wide limits, without breaking the chemical bonds. Structurally crystalline bundle can be distinguished from an amorphous bundle only by the fact that within the crystalline bundle there exists an azimuthal order in the distribution of the axes of the molecules and side groups. The degree of regularity in the amorphous bundle can vary within wide limits, in a number of cases approximating to the degree of regularity in the crystalline bundle. From these considerations it follows that there is a common mechanism for the transformation of structure during deformation of the crystalline and the amorphous polymer. The only difference is that with the crystalline polymer, to the energy of transformation of the amorphous structure is added the heat of fusion of the polymer crystals.

CONCLUSIONS

(1) The thermomechanical properties of crystalline and amorphous isotactic polystyrene have been studied and compared with the thermo-mechanical properties of ordinary atactic polystyrene. It has been shown that the vitrification temperatures of isotactic and atactic polystyrene are the same.

On the basis of the date obtained one can infer that during the making of products from a melt of isotactic polystyrene, to give them increased heat stability a subsequent heating above the vitrification temperature is necessary.

(2) It was found that crystalline isotactic polystyrene in an unoriented form is a very fragile material at ordinary temperatures owing to its high vitrification temperature (80°), lying above the usual range of working temperature for crystalline polymers.

(3) To get rid of the fragility of crystalline polymers, natural to them at temperatures below the vitrification temperature they must be preliminarily oriented.

(4) The nature of the dependence of deformation on the stress was studied for films of isotactic polystyrene over a wide range of temperature. It was shown that considerable deformation, accompanied by orientation of the samples, occurs only above the vitrification temperature of the polymer and has a relaxational character.

(5) The vitrification temperature and the size of the interval between it and the fusion temperature are very important characteristics for assessing the working properties of crystalline plastics and for finding rational methods for their treatment and use.

Translated by S. C. ALLEN

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THE INTERACTION OF PHENYL-β-NAPHTHYLAMINE WITH BENZOYL PEROXIDE AND THE EFFECT OF *O*-BENZOYL-*N*-PHENYL-*N*-β-NAPHTHYLHYDROXYLAMINE ON THE OXIDATION OF RUBBER *

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(*Received* 16 *September* 1958)

PHENYL-*β*-NAPHTHYLAMINE (Neozon D, PNA) is one of the most widely used antioxidants for rubber. However up to the present time there have not been sufficiently well founded ideas on the inhibiting action of this substance. It is to be assumed that the hydrogen of the imino group of PNA adds on to the active oxygen containing radicals of the rubber, as a result of which the oxidative chain is terminated. Proceeding from this hypothesis it may be deduced that the activity of an inhibitor increases with increase in mobility of the hydrogen atom of the imino group [1].

We have obtained data on the interaction of phenyl-*β*-naphthylamine with benzol peroxide (BP), which are of undoubted interest for the clarification of the action of PNA as an oxidation inhibitor. The reaction between PNA and BP was carried out at room temperature in ethereal solution at molecular ratios of 1 : 1 and 2 : 1. After mixing solutions of the reagents there appears first a brown, then dark violet coloration, showing the progress of the reaction. An increase in temperature of the mixture is observed, the main reaction time being 10–20 min. By analogy with the reactions studied by Gambarian [2] the process leads to the formation of benzoic acid and *O*-benzoyl-*N*-phenyl-*N*-*β*-naphthylhydroxylamine (BPNHA), according to the scheme:

$$(C_6H_5COO)_2 + NHR'R'' \longrightarrow C_6H_5COOH + C_6H_5COONR'R'', \qquad (I)$$

where R′ = phenyl, and R″ = naphthyl.

If the reaction between PB and PNA is carried out at a ratio of 1 : 1, then no other substances apart from benzoid acid and BPNHA are observed in the reaction mixture. At a ratio of 2 : 1 the reaction leads to the formation of benzoic acid in quantities greater than those corresponding to equation (I). Therefore it is to be assumed that the reaction in both cases is a free radical chain process, proceeding to the following scheme:

* Vysokomol. soedin. **1**: No. 1, 123–125, 1959.

$$ROOR + R'R''NH \longrightarrow \left[\begin{matrix} ROOR \\ R'R''NH \end{matrix}\right] \longrightarrow ROH + RO^{\cdot} + R'R''N^{\cdot} \qquad (II)$$

(Initiation of the chain)

$$RO^{\cdot} + R'R''NH \longrightarrow ROH + R'R''N^{\cdot} \qquad (III)$$

$$R'R''N^{\cdot} + ROOR \longrightarrow R'R''NOR + RO^{\cdot} \qquad (IV)$$

$$ROOR + R'R''NOR \longrightarrow \left[\begin{matrix} ROOR \\ R'R''NOR \end{matrix}\right] \longrightarrow 3RO^{\cdot} + R'R''N^{\cdot} \qquad (V)$$

(Growth of the chain)

$$RO^{\cdot} + R'R''N^{\cdot} \longrightarrow RONR'R'' \qquad (VI)$$

$$RO^{\cdot} + RO^{\cdot} \longrightarrow ROOR \qquad (VII)$$

$$R'R''N^{\cdot} + R'R''N^{\cdot} \longrightarrow R'R''NNR'R'' \qquad (VIII)$$

(Termination of the chain)

where $R = C_6H_5CO$, $R' = C_6H_5$ and $R'' = C_{10}H_7$.

At an equimolecular ratio of reacting substances reactions (VII) and (VIII) take place to a small extent, therefore the overall reaction corresponds to the stoichiometry of equation (I). With an excess of benzoyl peroxide the $RO^{\cdot}$ radicals accept hydrogen from the solvent, leading to the additional formation of benzoic acid.

The BPNHA obtained by us has, analogously to PNA, a vulcanizing effect on rubber by simultaneous action of BP and hydrogen sulphide. In connexion with this it could be suggested that the compound indicated is also capable of taking part in free radical processes of oxidation of rubber.

In fact, as may be seen from Fig. 1, BPNHA, when introduced into rubber in the quantity of 1 per cent, behaves as a strong inhibitor of the oxidation of the rubber. The induction period in the presence of the compound indicated exceeds by more than 3 times the induction period brought about by the action of PNA. The action of BPNHA depends on its concentration in the rubber ; at a low

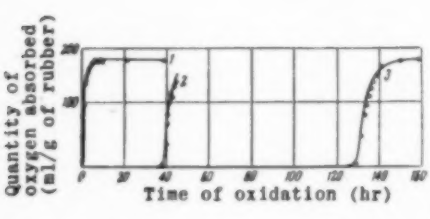

FIG. 1. Kinetics of oxidation of natural rubber at 140°: in the absence of inhibitor (1), in the presence of 1 per cent of PNA (2) and in the presence of 1 per cent of BPNHA (3)

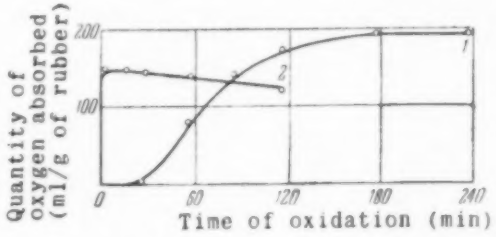

FIG. 2. Kinetics of oxidation of natural rubber at 140°: in the absence of inhibitor (1) and in the presence of 0·05 per cent of BPNHA (2)

concentration (up to 0·05 per cent) there is observed an accelerating action of this compound on the process of oxidation of rubber (Fig. 2).

Thus BPNHA, in spite of the absense from its molecule of imino hydrogen, is a stronger oxidation inhibitor than PNA. Its inhibiting action, apparently, is

bound up with its relatively easy break down into radicals, which than react with the active oxygen containing polymer radicals. It is also possible that, corresponding to the scheme of Boozer and Hammond, an intermediate radical complex is formed, in which the oxygen-containing polymer radical adds on to the amino nitrogen which possesses a lone pair of electrons. Both in the one or the other case the chain of oxidation of the rubber is terminated.

We are inclined to think that derivatives of hydroxylamine, analogous to BPNHA, might be formed by the oxidation of rubber in the presence of PNA, as a result of the interaction of the latter with stable peroxides of rubber or low molecular weight compounds formed in the reaction mixture. In such a case there will be observed the transition of PNA into a form which, from the point of view of inhibition of oxidation processes, is even more active. Such a process will naturally have an effect on the kinetics of oxidation of rubber.

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STUDY OF MACRORADICALS DURING POLYMERIZATION AND BREAKDOWN — I*

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(*Received* 19 *November* 1958)

THE concentration of free radicals during reactions in the liquid phase is of the order 10^{-8} mol/l. even in a relatively favourable case, for example, the radical polymerization of vinyl monomers. This concentration lies at the limit of possibilities of modern electron paramagnetic resonance spectrometers, even if the spectrum of the radicals under observation is a narrow one (about 1 gauss) and no paramagnetic saturation occurs with a super-high-frequency field energy density of the order of 0·001 erg/cm³. During reactions in highly viscous media, for example, during bulk polymerization, the life of free radicals, particularly polymeric ones, is increased, and the method of electron paramagnetic resonance may be effectively used to study such important reactions as the final stages of polymerization and vulcanization.

In the present work this method has been used to study the polymerization of methylmethacrylate.

EXPERIMENTAL

The paramagnetic spectra were measured on a spectrometer, already described in its general features [1].

A band-pass resonator type H_{011} was used in the apparatus, as well as a platinum bolometer, connected to a resonance intensifier and phase-sensitive detector. The magnetic field of the electro-magnet was stabilized with an accuracy of 10^{-5} by means of an electronic current stabilizer. The spectrum was recorded on an EPP–09 recording device.

The layout of the auto-tuner of the klystronic generator was similar to that described by Veselago and Irisova [2]. A low inertia circuit (see Fig. 1) was used to effect thermostatic control of the specimens. A Teflon (PTFE) tube with an external diameter of 7 mm and walls 0·5 mm thick, into the centre of which a quartz

* Vysokomol. soedin. **1**: No. 1, 132–137, 1959.

ampoule containing the specimen was inserted, was located along the axis of the resonator. Air, heated to a given temperature by means of a Nichrome coil, was blown into the gap between the ampoule and the tube at a fairly rapid rate. A chromel-copel thermocouple was used as a temperature gauge and heating was continuously controlled by means of a device consisting of a redesigned EPV–01 automatic electronic potentiometer and an electro-magnetic amplifier.

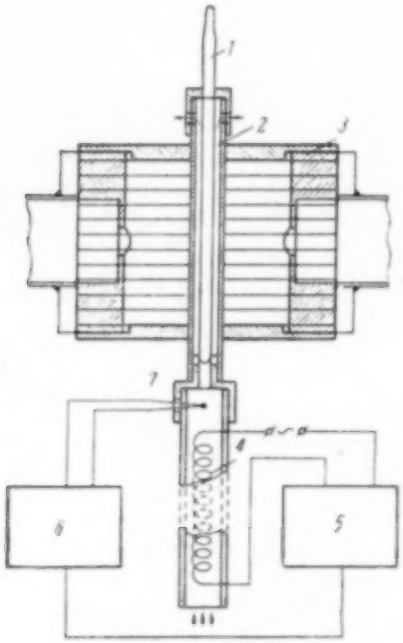

FIG. 1. Construction of resonator and thermostatic control of the specimen: 1 – quartz ampoule, 2 – tube of PTFE, 3 – resonator, 4 – Nichrome coil, 5 – electro-magnetic amplifier, 6 – EPV-01 automatic potentiometer, 7 – thermocouple.

To reduce vibrations of the resonator caused by induction currents in its walls, at the frequency of modulation of the magnetic field, such currents restricting the permissible amplitude of modulation, the resonator was constructed of brass plates 4 mm thick insulated from each other by thin sheets of mica.

The natural quality of such a resonator is ~ 10,000 c/s and the limiting sensitivity of a spectrometer with such a resonator with a constant time of 30 sec is equal to $3{\cdot}5 \times 10^{-12}$ mole of crystalline diphenylpicrylhydrazyl (DPPH).

To determine the sensitivity of the spectrometer from crystalline DPPH, fairly small specimens (of the order 10^{-11} to 10^{-12} mole) had to be obtained. In preparing mixtures containing such small amounts of DPPH, the latter was partially destroyed. In addition, different specimens showed spectrum lines of

different width. Graduation using a solution of DPPH is more correct, though even in this case error may arise due to the effect of oxygen, light, and other additions contained in the solvent, on the DPPH. To determine sensitivity, therefore, we used the following method: successive dilutions in benzene were made of an initial solution with a concentration of 1 mg/ml. Specimens of varying concentration were thus obtained and their spectar recorded. Figure 2 shows the dependence of the signal of paramagnetic absorption (U) on the amount of DPPH (μ).

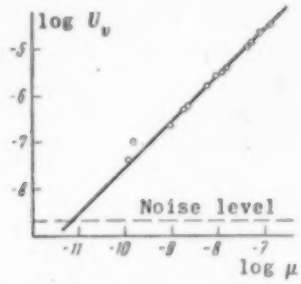

FIG. 2. Calibration of spectrometer.

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It can be seen that the proportionality between U and μ is maintained even with extremely small amounts (~ 10^{-10} mol). It is therefore justifiable to record the spectrum of a comparatively large amount of crystalline DPPH, with reduced sensitivity of the intensifier, and extrapolate the resulting signal to the maximum sensitivity determined by the "noise" of the apparatus.

In practice the spectrum was obtained with 10^{-8} mol of DPPH. The noise of the apparatus was then recorded and the limiting sensitivity calculated (i.e. the amount of DPPH which gave a paramagnetic absorption signal equal to the noise level). Figure 3 shows the spectrum of a specimen containing $1{\cdot}1 \times 10^{-10}$ mole

FIG 3. Spectrum of $1{\cdot}1 \times 10^{-10}$ mol. DPPH dissolved in benzene.

DPPH dissolved in benzene. The spectrum was obtained with a constant time time of 4 sec using the resonator previously described. The graduation conducted using the resonator, which had a quality $Q_0 = 22{,}000$, gave the value of limiting sensitivity as 2×10^{-13} mol DPPH.

TEST RESULTS

Measuring the course of polymerization by the dielectric losses

One difficult problem in studying polymerization is that of measuring moderate and high degrees of conversion.

The normal dilatometric method was not practicable due to the high viscosity of the system and in polymerizing methylmethacrylate we used a convenient method — that of measuring dielectric losses. A quartz ampoule containing the polymerization system was placed inside a volumetric resonator tuned to a wavelength of 3·2 cm, excited by means of a standard generator. The intensity of the electro-magnetic field in the resonator was recorded by means of a detector crystal loosely linked to it and connected to a galvanometer.

As polymerization progressed the dielectric losses in the specimen decreased, since the angle of losses in polymethylmethacrylate at super-high frequencies is two orders lower than those in the monomer. Because of this the quality of the volumetric resonator was increased, and consequently the strength of the electromagnetic oscillations passing through the resonator to the detector crystal at the point of resonance also increased. By disregarding the dielectric losses in the polymer, compared with those in the monomer, and assuming that the losses in the specimen were proportional to its monomer content, it was possible to determine the degree of conversion without using any additional calibration.

Let us denote the resonance coefficient of transfer * through the resonator containing the empty ampoule by T_0, the coefficient of transfer through the resonator containing the ampoule with the initial monomer by T_1, and that of the same ampoule some time after polymerization has commenced when the degree of conversion must be measured by T_x. Using an equivalent system [3] we obtain the relation:

$$\alpha = (1 - \sqrt{T_1/T_x}) / (1 - \sqrt{T_1/T_0}) \qquad (1)$$

where α is the degree of conversion (polymer content) per cent.

For increased accuracy in measuring the coefficient of transfer the power falling on to the detector crystal was always reduced to the same value by varying that coming from the generator by means of a calibrated attenuater; the accuracy of the method was ± 2–3 per cent.

The original assumptions were checked by comparing the amount of polymer calculated according to formula (1) with that directly detected. For this purpose polymerization was interrupted, the ampoule opened and its contents dissolved in benzene. After cryosublimation under reduced pressure the amount of polymer remaining was determined by weighing; the results of the comparison are given in Fig. 4.

Macroradicals in the polymerization process

A commercial monomer was freed from inhibitor by the ordinary method and was then distilled *in vacuo* in a quartz ampoule of internal diameter 3 mm. Photopolymerization of methylmethacrylate was carried out outside the resonator at

* The coefficient of resonance transfer is the ratio of the power passing through the resonator at the moment of resonance, to that entering it from the direction of the generator.

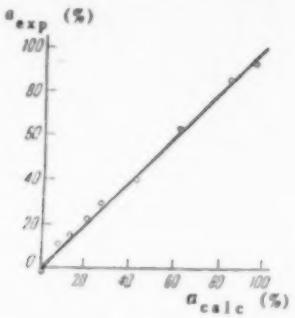

FIG. 4. Check on method of determination of depth of polymerization from dielectric losses.

25°C using light from a PRK-4 mercury lamp, passed through a water filter. In some cases butyl bromide was used as a sensitizer. After definite lapses of time we measured the dielectric losses and recorded the paramagnetic absorption spectrum. A typical curve for the polymerization and accumulation of radicals is shown in Fig. 5, in this case for unsensitized photopolymerization. The absolute concentration of radicals was determined by double integration of the curves and comparison with the corresponding values obtained by calibration with crystalline DPPH (see above).

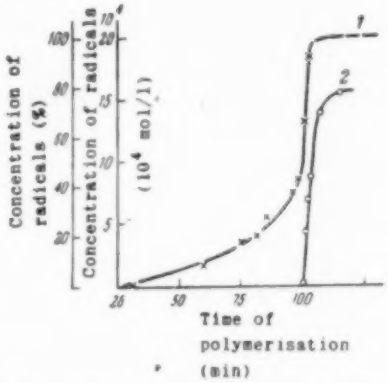

FIG. 5. Kinetics of photopolymerization of methylmethacrylate. (1) Depth of polymerization; (2) Concentration of radicals.

The spectrum observed did not differ from that of the radicals trapped in the polymer during polymerization of methylmethacrylate in a precipitator and described by Ingram *et al.* [4] (Fig. 6a). It consists of 5 main lines with interval ~ 26 gauss and ratio of intensity 1 : 4 : 6 : 4 : 1, which corresponds to equal interaction of the unpaired spin of the electron with the magnetic moments of the four protons. Ingram gives a possible explanation of this fact [4]. The origin of the four intermediate weak lines is still not clear.

FIG. 6. Electron paramagnetic spectrum of 'trapped' macroradicals and of their change on heating. (a) Original spectrum; (b,c,d) Spectra at subsequent instants.

In order to determine the life of the radicals at the various stages of polymerization, polymerization was broken off and we determined the rate of polymerization and the rate of decrease in the concentration of the radicals in the dark. It was found that with depth of polymerization 60 per cent and above the rate of polymerization in the dark is very much lower than we might expect from the existing concentration of macroradicals in the system, and falls to zero in a few minutes after the cessation of illumination, although the concentration of radicals falls in this time by 15–20 per cent at the most. At the same time there also ceases the reduction in the concentration of radicals. The remainder of the radicals are relatively stable and are incapable at room temperature either of recombination or of combination of the monomer. If the system is once again irradiated, then polymerization again proceeds at a high rate.

Thus the spectrum observed relates mainly to the trapped macroradicals, whose concentration is only indirectly related to the kinetics of polymerization. It is possible that this stability is a consequence of the difficult accessibility of the reaction centres of these radicals (whose structure is normal in all other respects), thanks to their high molecular weight and coiling of the chain.

An attempt was made to trace the fate of the trapped radicals on heating of the polymer. It was found that even at 60°C the spectrum alters at a considerable rate. The intensity of the four weak intermediate lines of the spectrum increases with the diminution of the five main lines (Fig. 6, b, c, d). Finally, these latter disappear altogether and we are left with a spectrum with four lines spaced at ~ 25 gauss and corresponding to interaction of the unpaired electrons with three protons.

One possible assumption is that at high temperatures the trapped radical is capable of scission of the comparatively weakly bound hydrogen from the CH groups in the vicinity of the unsaturated ends of the molecules of the polymer which are formed as a result of disproportionation :

$$-CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}\cdot \;+\; \underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}=CH- \rightarrow -CH_2-\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}} \;+\; \underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}=C\dot{-}$$

the unpaired electron in the new radical which is formed interacts wich the three protons as a result of conjugation. Simultaneously with the transformation of the spectrum there is a decrease in the total number of radicals, but at each given temperature only a portion of them are instable; the remainder are relatively stable and disappear only on further raising of the temperature (Fig. 7). Above T_g the spectrum disappears altogether.

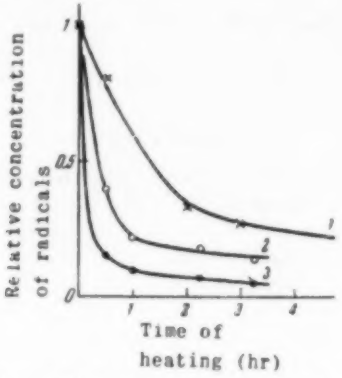

FIG. 7. Kinetics of reduction in concentration of 'trapped' radicals on heating (1) in polymer prepared without sensitizer at 60°C; (2) in polymer prepared without sensitizer at 80°C; (3) in polymer prepared in presence of 1·5 per cent butyl bromide at 80°C.

An interesting feature in this phenomenon is that the transition from macroradicals of the first order (with 5 lines) to radicals of the second order (with 4 lines) is accelerated if there are low-molecular admixtures in the polymer, for instance remains of sensitizer (butyl bromide) or traces of oxygen (see Fig. 7). This shows that the scission of hydrogen is effected not directly, as described above, but by transfer of the reaction centre by low-molecular substances.

On investigating the spectrum of the radicals of polymethylmethacrylate it was found that saturation sets in already at an energy density of the magnetic field in the resonator of the order of 10^{-3} erg/cm^3 (i.e. under the present conditions at a power of the super-high-frequency generator of the order of tens of mW). The time for thermal relaxation found from this, T_1, is of the order of 10^{-5} sec, i.e. unusually high for free radicals (usually it is of the order of 10^{-8} sec).

To retain the possibility of absolute calibration the paramagnetic spectra for the investigation of the kinetics were recorded at low powers of the generator (of the order of 1 to 0·1 mW).

In conclusion we must thank B. L. Erusalimskii for his assessment of the results.

CONCLUSIONS

The use of a sensitive electron paramagnetic spectrometer has made it possible to produce a number of new quantitative and qualitative data on the kinetics of polymerization and the behaviour of macroradicals at great depths of polymerization. In particular it is shown that in block photopolymerization of methylmethacrylate there accumulate a considerable number of trapped macroradicals.

From investigation of the changes in the spectra on heating, conclusions are drawn as to the secondary reactions of these radicals and on the influence of low-molecular admixtures upon the rate of these reactions.

Translated by R. J. MOSELEY

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CURRENT EVENTS

TENTH ANNIVERSARY OF THE INSTITUTE OF HIGH MOLECULAR COMPOUNDS OF THE U.S.S.R. ACADEMY OF SCIENCES

SIXTH (JUBILEE) CONFERENCE OF THE INSTITUTE*

SCIENTIFIC sessions of the Institute of High Molecular Compounds of the U.S.S.R. Academy of Sciences, dedicated to the tenth anniversary of the Institute, took place in Leningrad in the large conference hall of the Academy of Science from 13 to 17 January.

The Institute of High Molecular Compounds of the U.S.S.R. Academy of Sciences [I.V.S. AN U.S.S.R. (Inst. of High Molecular Compds. U.S.S.R. Akad. Nauk)] was organized on 15 June 1948 in fulfilment of the resolution of 7 July 1947 of the Committee of Ministers of the U.S.S.R. From the moment of its formation the Structure of the Institute envisaged a closely linked physical and chemical investigation of polymers. Originally this establishment was fixed as the staff of five chemical and two physical laboratories directed by corresponding members of the Akad. Nauk U.S.S.R. — S. N. Ushakov, S. N. Danilov, N. I. Nikitin and Professors V. A. Dolgoploskii, A. A. Vansheidt, M. V. Vol'kenshtein and V. V. Tsvetlov.

In the first period of its existence the Institute's activities were apportioned to a series of university laboratories. In 1952 a group of eminent specialist members in the field of the chemistry and physics of polymers transferred from the Physico-technical Institute to the I.V.S.: corresponding member of the U.S.S.R. Academy of Sciences, P. P. Kobeko, Professors M. M. Koton, E. V. Kuvshinskii, G.P. Mikhailov and S. E. Bresler with groups of their chief co-workers. In this year also all the laboratories of the Institute were concentrated in one building as a result of the completion of building work.

The growth of the Institute is continuing. At the present time it consists of 11 laboratories (five chemical, two physico-chemical and four physical) and two independent groups.

Since 1952 an annual scientific conference of the I.V.S. has been organized, summing up the scientific activities of the Institute for the year. These conferences invariably led to the attraction of representatives of allied academic and associated institutes and representatives of industry. Thus, the practical form of the report by the Institute promotes the consolidation of links with industry and the co-ordination of scientific investigations.

At the jubilee meeting, the sixth conference was contributed to by about 400 persons among whom were representatives of the scientific and industrial establishments of Moscow, Sverdlovsk, Dzerzhinsk and other cities. 120 participants at the conference came from towns other than Leningrad.

In his introductory words, the director of the Institute, corresponding member of the U.S.S.R. Academy of Sciences, Professor S. N. Danilov briefly reminisced about the

* Vysokomol. soedin. 1: No. 1, 166–172, 1959.

scientific path taken by the Institute over 10 years and described the new problems placed before the Institute.

Below is given a brief survey of the reports given before the conference.

I

Six reports were heard at the plenary meeting devoted to the mechanism of radical reactions.

In the report of S. E. Bresler, E. N. Kazbekova, and E. M. Saminskii — Investigation of macroradicals in polymers by the electron paramagnetic resonance spectroscopy — it was shown that in the polymerization of a series of monomers, part of the macroradicals are "frozen" and become capable only of recombining or of addition to monomers at a low ratio of conversion (40 per cent). At higher temperatures these radicals "revive" and enter into a series of reactions, on the mechanism of which some assumptions are made. However, in polymethacrylic acid these reactions go with difficulty even on heating to 140–180°, since diffusion is hindered by the reversible formation of hydrogen bonds.

The free radicals arising from mechanical destruction of the polymer were also investigated by EMR. They were defined quantitatively and assumptions were made on the condition of these radicals. They could be used as a convenient model for the investigation of reaction ability.

The report of M. P. Vershinin was also devoted to the mechanical destruction of polymers. The destruction was produced on a turning machine tool by removing shavings under conditions excluding thermal effects. A diminution of the average molecular weight of polymethylmethacrylate and polystyrene was observed approximately proportional to the size of the surface of the shaving removed, from which the conclusion was made that macromolecules are broken by the action of splitting strains brought about by planes.

The report of G. M. Chetyrkin, M. M. Koton, T. A. Sokolov and V. N. Nikitin was devoted to a study of the polymerization of a series of *N*-substituted phenylmethacrylamides with various substituents in the phenyl residue. The authors showed that the presence of intermolecular hydrogen bonds, detected by IR-spectroscopy, in *m*- and *p*-*N*-substituted phenylmethacrylamides retarded the speed of polymerisation by comparison with the ortho-isomers, the molecules of which are not associated.

The report of B. A. Dolgoploskii, Zh. D. Vasiutin and G. P. Belonovskii was devoted to the mechanism of the inhibitory action of polyphenols and the role of oxygen in the polymerization process. In the report the influence of the oxidation-reduction potential on the inhibitory activity of polyphenols and corresponding quinones was discussed and the phenomenon was elucidated, in connexion with oxygen in the system. For example, ditertiarybutylhydroquinone showed experimentally that the inhibitory activity of polyphenols in the presence of oxygen is connected with the formation of a stable semiquinonoid radical RO_2 on account of the oxidation of the polyphenol.

B. A. Dolgoploskii, B. L. Erusalimskii, T. N. Kuren'gina and E. I. Tiniakova in a report "Mechanism of the destruction of polymers under the influence of free radicals", showed that rupture of C—C bonds in the polymer chain under the influence of free radicals is a two stage process: at first the free radical abstracts an atom of hydrogen or (if the principal valency link contains double bonds) it combines with the double bond. In either case this leads to the formation of a polymer free radical. Subsequently, at sufficient dilution it disintegrates, one of the two new formed chains retains free radical character, but the second is stabilized owing to the appearance of a double bond. In highly concentrated systems the disintegration reaction of the polymer radicals competes with recombination.

In the report of A. T. Os'minskii, A. G. Popov and G. P. Belonovskii "Thermal destruction of methylmethacrylate copolymers" some factors were revealed which permit the raising of the thermal stability of polymers. One of these is the artificial arresting of kinetic

chain depolymerization which is achieved by introducing additives into the polymer mass, trapping free radicals, or by introducing hetero-groups into the homopolymer chain. Another possibility consists of a preliminary heating of the homopolymer (polymethacrylic acid, polymethacrylamide) side groups of which are able to condense: in this way, partial destruction is accompanied by the formation of hetero-rings, strengthening the chain.

II

The report of A. A. Korotov, S. P. Mitsengendler and V. I. Krasulinova on "The Preparation of crystalline polymethylmethacrylate" was read at a plenary session. The authors showed that isotactic PMMA (polymethylmethacrylate) could be obtained by polymerization, catalysed by butyl lithium in toluene solution at temperature of the order of $-50°$. The type of stereoregulation depends on the catalytic complex, which in its turn, is influenced by the solvent. In nonpolar solvents electrostatic interaction of the catalyst with the carboxylic acid monomer forces the formation of a new bond always at the same isotactic position. In polar solvents, for example pyridine, this is not the situation, and owing to free orientation of the associated monomer relative to the stump end of the chain the energetically very satisfactory syndiotactic addition occurs. The vitrifying points (T_c) of both types of PMMA are accordingly 52–62° and 128–135°, in agreement with published data of foreign investigators. It is interesting that only isotactic PMMA crystallized in each case, if the precipitate was produced in a saturated hydrocarbon (hexane); precipitation in methanol led to irreversible formation of an amorphous structure. In the discussion (O. B. Ptitsyn, S. Ia Frenkel') the assumption was stated that this was explained by specific action of the precipitant. In the first case it is not influenced by the hydrophobic suspended PMMA and it strengthens the interaction of the polar groups; the polymer comes out of this unfolded chain; on the other hand, methanol (and possibly every other polar precipitant) gives rise to a kind of "globulization" (by analogy with proteins) by which PMMA comes out of solution in the form of compact lumps with the hydrophobic group oriented inwards and the polar (solvated with precipitant) outwards.

In the report of B. A. Dolgoplosk11, E. I. Tiniakov, A. I. Maveia, M. Z. Al'tshuler, T. G. Zhuravlev and R. N. Kovalevskii on "The synthesis and study of crystalline and amorphous transpolymers of dienes on oxide catalysts" the possibility of obtaining crystalline *trans*-1 : 4-polymers of isoprene and butadiene with the help of catalysts like chromic oxide on aluminosilicate was pointed out. Any break in the regularity of the chain (for example by the introduction of a foreign monomer) led to the elimination of crystallinity and the formation of rubber-like polymers by preservation of the *trans*-structure of the chain.

T. M. Birshtein and O. B. Ptitsin in a report on the "Theory of dimensions, dipole moments and optical anisotropy of stereospecific macromolecules" showed, on the basis of calculations taking into account the correlation between conformation of adjacent monomers in the chain, that the physical properties of macromolecules in solution were sensitive to the stereoisomeric structure of the chain. These theoretical considerations were confirmed by the work of V. N. Tsvetkov and S. Ia. Magarik, communicated in the report, "Dynamic doubly refractive solutions of isotactic polystyrene in bromoform". The authors discovered considerable differences in the optical anisotropy of molecules of isotactic and atactic polystyrene. On this basis a method could be proposed for the quantitative estimation of chain stereoregularity of polymers.

Another possibility for the experimental analysis of the character and chain regularity of polymers by IR-dichroism was indicated in the interesting report of Iu. Ia. Gotbil on "The Intensity of Polarization and Infra-red Dichroism in the Vibration Spectra of Spiral Polymers". Correlation between the dichroism of different bands could be linked with the chain stereoregularity of polymers. The report of E. I. Pokrovskii, "The Infra-red Spectra

of Stereoregular Polymers" (polypropylene, polystyrene and PMMA) was devoted to the question of quantitative determination of chain crystallinity.

The discussion on the second group of papers, in which S. E. Bresler, M. V. Vol'kenshtein, V. N. Tsvetkov, O. B. Ptitsin, B. A. Dogadkin, P. I. Zubov and others took part, touched on the basic possibility of analysing the stereoregularity of chains by the basic properties of individual molecules. In particular, the opinion was expressed (M. V. Vol'kenshtein, S. E. Bresler) that in teta-point one can demonstrate the spiral character of stereoisomeric chains. Evidently unanimity was not attained on this question. (Further discussion on the behaviour of polymers at the teta-point was continued in the final meeting).

III

In the chemical section, with the theme "Investigations in the field of synthesis of monomers and polymerization" the report of A. A. Korotov, I. S. Lishansko, A. G. Zak and E. F. Federov on "Polymerisation of Pentene-1 with Complex Catalysts" was read. The authors worked out the method and studied the polymerization of pentene-1 under the influence of $TiCl_4-Al(C_2H_5)_3$ catalyst in the temperature range 20–50°. A rubber-like polymer was obtained similar in properties to poly*iso*butylene.

Discussion was provoked by the report of S. E. Bresler, M. I. Mosevitsko, I. Ia. Poddubnii and Shi Guan — "Study of Polymerization on Ziegler Catalysts by EMR Spectroscopy and Kinetics" in which the non-radical nature of this polymerization was shown and the observed EMR spectra were interpreted in terms of the formation of a paramagnetic (partly reduced) titanium ion. The possibility of observing false EMR spectra at room temperature was explained by the influence of Al and Li atoms on the electric field of the titanium chloride lattice in consequence of chemisorption of corresponding organometallic compounds on its surface.

V. V. Voevodskii did not object in principle to a similar interpretation and cited another example — this time with a homogeneous (solution) Ziegler catalyst — in which the EMR spectrum observed could be attributed to signal splitting from a radical (or ion-radical) atom of aluminium. K. S. Minsker quoted experiments in which it was shown that the usual inhibitors of radical polymerization had no influence whatever on the polymerization under the action of Ziegler-Matta catalysts; this excludes the possibility of a radical chain reaction. S. E. Bresler supported this point of view.

B. A. Dolgoploskii, Van Po-sun and B. L. Erusalimskii reached the conclusion that radical stages were absent in systems of like character. This was put forward in the paper "Study of the Reaction between Ethylmagnesiumbromide and Salts of Heavy Metals". They showed that free radical acceptors (styrene, α-methylstyrene) did not influence the yield of ethane and ethylene made by the interaction of ethylmagnesiumbromide with salts of titanium and cobalt.

A series of reports was devoted to the preparation and characterization of new monomers and polymers.

T. B. Sheremetevo and G. I. Lapino presented a report on "The Synthesis of some Unsaturated Nitrogen Containing Cyclic Compounds". The authors made and characterised a series of new *N*-alkylsubstituted imides of citraconic acid, specifically the *N*-methyl-, ethyl-, *iso*propyl-, butyl-, octyl- and *cyclo*hexyl-derivatives. Use of a new method of synthesis permitted a considerably higher yield of the corresponding product in some cases. N. S. Sidorova, G. E. Ustiozhanin and G. A. Efirmova in their paper "Aminoderivatives of the anhydride of xylite" reported on the elaboration of methods for the introduction of aminogroups into the xylite molecule and an aminoxylite, using aminated ammonia, aliphatic and aromatic amines. In this work the reactions of the tosyl esters of xylite dianhydride with various amines were also studied, permitting the synthesis of a series of aminodianhydroxylites and diaminoanhydroxylites.

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Iu. V. Mitin and M. M. Koton in a paper on "The Polymerization of dialdehydes" reported the first results of the use of the Cannizzaro–Tishchenko reacting for making polymers. By carrying out the condensation in the presence of aluminium ethoxide, polymers of *tere*phthalyl-*iso*phthalyl- and diphenyl-dialdehydes were made. The molecular weight of poly*tere*phthalyldialdehyde reached 100,000–200,000. The structure of the polymer was demonstrated by the hydrolytic degradation method.

In the report "Synthesis of polymeric hydrocarbons of the poly*para*xylylene type from dichlormethyl derivatives of aromatic compounds under the influence of metallic sodium" (authors A. A. Vanshteidt, E. P. Mel'nikova, L. V. Kukhareva, and M. G. Krakoviak) it was shown that linear polymers with rings on the basic chain could be obtained in high yield (up to 80 per cent) by using the Wurtz reaction in dioxan solution with finely divided sodium. In particular this route was used for the synthesis of polymers from *p*-xylylenedichloride, 4, 4′-*bis*chloromethyldiphenyl, 4, 4′-*bis*chloromethyldiphenylmethane and others.

M. M. Koton, T. M. Kiseleva, N. P. Zapevalova, P. A. Paribok and V. S. Florinskii presented a report — "Synthesis and Polymerisation of Metal Containing Styrenes and Methacrylates" in which they announced the synthesis of methacrylic esters of trialkyl (or aryl) derivatives of tin and metal-containing styrenes (Pb, Bi, Sn, Hg, and others) capable of polymerization. Polymers of the first type, depending on the length of the alkyl substituent, can be glass like (methyl, ethyl-, propyl-) or rubber-like (butyl- and higher) polymers. Metal containing styrenes were polymerized in the solid and in solution and copolymerized with styrene and methylmethacrylate with formation of transparent thermoplastic polymers.

In the paper of E. M. Kazbekov, S. E. Bresler and E. M. Saminskii "A New Method of Studying the Kinetics of Polymerization by Dielectric loss", a new and extremely convenient method for investigating the kinetics of polymerization was proposed, based on the sharply different (in the S. V. Ch. range) dielectric properties of the free monomer and its polymer.

The diminution of the dielectric loss with growth of the chain is conversly recorded by increasing S. V. Ch. power, passing through a tuned resonator with a frequency of 10^{10} c/s, in which the ampoule with the polymerization system is placed.

IV

In the physical section (the mechanical and dielectric properties of polymers) the paper of M. V. Vol'kenshtein — "Towards a Theory of High Elasticity of Polymers" was devoted to the substantation and development of the ideas of V. A. Kargin on block structure of amorphous polymers in the theory of high elasticity. For the description of high elasticity the analogy between polymers and ferromagnetic substances seems very fruitful.

Speaking in the discussion G. M. Bartenev spoke on the possible links between bundles and rods, formed by breakage. G. L. Slonimskii remarked that already the semiquantitative calculation led to better agreement with experiment than the gas model. T. M. Khazanovich pointed out the necessity of calculating the volume effect for swollen resins.

In the report of G. A. Lebedev and E. V. Kuvshinski "Establishment of the High Elastic Deformation of Amorphous Materials of the PMMA Type, Found in the Solid State" the existence of rubber-like elasticity was shown close to Tc, the observation of which, however, is complicated by the formation of a neck, that gave cause for a series of authors to accept the corresponding deformation as plastic.

In the paper of M. I. Bessonov and N. P. Kuznetsov on "Creep and Synthetic Fatigue in Orientated PMMA" it was shown in detail that increase in chain stretching leads to a sharp increase in the mechanical durability of the material and a complicated regularity of static fatigue. The reports of S. K. Zakharov, and E. V. Kuvshinskii "Influence of Orien-

tation on the Mechanical Properties of some Polymeric Materials" and of E. V. Provotorovo, G. A. Lebedev and E. V. Kuvshinskii on a "Method of Characterizing Plane-orientated Material by the Property of Optical Anisotropy" were devoted to the problem of using orientated polymers as constructional materials and structural analysis of these polymers.

In the paper of G. P. Mikhailov and T. I. Borisov on "Dielectric Relaxation in Copolymers of Methylmethacrylate with Styrene" it was shown that in polymers at one and the same temperature, two independent relaxation spectra co-exist, according with dipole-radical and dipole-elastic losses. Owing to differences in the temperature coefficients, these relaxation processes were observed separately or superimposed one on the other, depending on the ratio of the appropriate relaxation times. In the temperature-frequency fields above this where the relaxation times of both processes are levelled out, relaxation dielectric losses of only one type are always observed experimentally. The dependence of the effective dipole moment of the copolymer on the content of methylmethacrylate shows that in the vitreous state an increase in concentrarion of the polar component leads to intermolecular interaction but in the high elastic state to intensification of intramolecular coupling of dipole groups. The discussion of this paper (Iu. S. Lazurkin, G. L. Slonimskii, M. V. Vol'kenshtein) was devoted, basically, to the physical meaning of the apparent energy of activation for relaxation processes in polymers.

V

In the plenary session devoted to vitrification and softening, A. V. Sidorovich and E. V. Kuvshinskii in a paper on "The Study of Glassy Polymers on Heat Expansion" developed the phenomenological relaxation theory of heat expansion of amorphous substances. The differential equation for thermal expansion takes into account the dependence of the volume relaxation time both on the temperature and on the volume. The theory was checked with experiments on polystyrene.

E. V. Anufrieva and M. V. Vol'kenshtein in a communication on "Investigation of glasses by the method of luminiscence" suggested the use for analysis of broken glasses of the change in intensity either of fluorescence by introducing a fluorescent substance into the polymer (necessarily without a rigid skeleton) or phosphorescence with a luminescent compound. The authors presented data obtained for PMMA, polyvinylchloride, polystyrene and polyvinyl alcohol.

In the report of Iu. A. Sharonova and M. V. Vol'kenshtein on the "Thermal heat capacity of amorphous polymers" was described a precision method of heat measurement permitting the exposure of the relaxation character of softening of glassy polymers and the dependence of the process on the annealing time of the polymer in the glassy state and on the rate of heating.

The discussion on these three papers studied the ways of making more accurate the systematics and terminology of the matter. E. V. Kuvshinskii thought that available experimental material was insufficient for the creation of any adequate molecular theory, and recommended, at the present stage, the organization of a phenomenonological theory, working only with values directly resulting from experiment. M. V. Vol'kenshtein considered that the molecular theory of glasses put forward by himself and O. V. Ptitsin was fully identical with the phenomenonological theory of E. V. Kuvshinskii and A. V. Sidorovich. G. M. Bartenev turned his attention to this, that one ought to distinguish the concepts of heat and frequency vitrification. Objecting to this, M. V. Vol'kenshtein noted that the fragility of fluids, revealed by the influence of fast loading (in frequency, periodicity) was an excellent basis for the appearance of vitrification and softening, to a discussion of which the papers were devoted. G. P. Mikhailov thought the method of variation of chemical composition of the polymer could give valuable information on the mechanism of vitrification.

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In the paper of L. M. Pirkov on "Physico-chemical Methods for the Investigation of Hybrid Polymers", for example the block-polymer of isoprene and styrene made by A. A. Korotkov and L. A. Shibaev, methods of investigation were exhaustively demonstrated, offering a whole series of successive tests — selective extraction, turbidimetric titration, U. V. analysis, pyknometric and refractometric analysis and so forth.

VI

The concluding plenary session was devoted to the problems of sorption and the state of macromolecules in solution. G. V. Samsonov's paper was devoted to the first problem, with the theme "Complementary Interaction of Absorbed Ions on Organic Substances". In it was reported a new phenomenon: the participation of hydrogen bonds in sorption (for example in penicillin anionate). This phenomenon opens a whole series of new technical possibilities.

Several reports were devoted to the second problem.

In the paper of V. N. Tsvetkov and S. Ia. Lubino "On the Influence of Solvents on the Form Effect in Polybutylmethacrylate Solutions", it was simply shown that the volume effect (long range action) in solutions considerably alters only the dimensions of linear macromolecules, whereas the asymmetric form of molecular spheres is not dependent on the solvent.

V.N. Tsvetkov and S. I. Klenin, in a paper on "The Concentration Dependence of the Diffusion Coefficient in an Ideal Solution", in the system polybutylmethacrylate *iso*propanol, demonstrated the absence of this dependence at a concentration < 1 per cent. The increase of D with concentration was usually observed in this form in large solvents resulting from the thermodynamic interaction with the solvents, whereas hydrodynamic factors play a considerably smaller part.

V. E. Eskin and O. Z. Korotkina gave a paper on "Light Dispersion and Viscosity of Solutions of Poly-β-vinylnaphthalene". In benzene for this polymer $[\eta]=0{\cdot}17\times10^{-4}\,M^{0{\cdot}8}$ dl/g, at the anomalously low value for the "Florey constant" of $F=(0{\cdot}5\text{–}1{\cdot}0)\times10^{21}$. The swelling parameter was also rather low: $a=1{\cdot}2$. Because of the large value of the exponent in the formula for $[\eta]$ and the very large size of the spheres in benzene and a mixed solvent of toluene with dekalin (1 : 1·3) by comparison with polystyrene, one ought to attribute the high thermodynamic rigidity of the chain to the result of the substitution of a naphthalene dicycle for a benzene ring.

Another "protein like" type of rigidity was described in the communication by V. G. Aldoshin, S. Ia. Frenkel and G. M. Chetyrkina on "Hydrodynamic Properties of Some Vinyl Polymers with Intra-molecular Hydrogen Bonds". For poly-*p*-carbethoxylphenylmethacrylamide in acetone the authors discovered the relation $[\eta]\sim M^{1{\cdot}35}$ capable of occuring only for rigid asymmetric particles. This rigidity is cased, evidently, by the formation of linear hydrogen bonds, parallel to the long axis of the macromolecule. "Denaturation" of this polymer in a mixture of dimethylformamide and formamide (7 : 3) converted it into a normal lump with $a=0{\cdot}8$ (the exponent in the formula for $[\eta]$). Transition of another type — rigid globules — to lumps was observed on "denaturation" in dimethyl formamide of the copolymer of MMA and methacrylic acid (9 : 1).

These processes could serve as a simple method for very complicated intramolecular conversions it was reported in the paper by S. E. Bresler, V. P. Kushner and S. Ia. Frenkel' on "Investigation of Transformations of the Order-disorder Type in Some Globular Proteins". By selective variation of solvent or by chemical modification of a series of proteins all kinds of intramolecular "solution" and "melting" of separate elements of the structure of the macromolecule could be observed. In this, one and the same kinetic (dynamic) particle could take the form of a rigid spheroid, a rigid linear molecule, a static lump or a linear polyelectrolyte.

S. E. Bresler, V. N. Tsvetkov, O. B. Ptitsin, C. Ia. Frenkel', V. E. Eskin and others took part in the general discussion on the last group of papers. It was concerned with the basic problem of "partial solubility" of macromolecules, i.e. the heterogeneous interaction of the different side groups of a single polymer chain with the solvent. This circumstance, displayed especially strikingly by precipitated block-polymers in various solvents, can complicate the problem of determining the probable size of macromolecules, especially in mixed solvents. The possibility of revealing the specific interaction of different groups of macromolecules with solvents was discussed.

Translated by M. J. NEWLANDS

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INVESTIGATION OF THE ANISOTROPY OF ELECTRICAL CONDUCTIVITY OF POLYMERIC ELECTROLYTES*

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(*Received* 9 *July* 1958)

INVESTIGATION of the processes of orientation of polymers is of great practical and theoretical interest.

At the present time it may be considered to be established [1,2] that the mechanical and structural anisotropy arising during the orientation of polymers does not always lead to strengthening of intermolecular interaction and to an increase in the packing density of the chains.

The change in the packing density of polymers on orientation depends mainly on the flexibility of the chains and on the nature of the intermolecular interaction, and also on the kinetics of the processes of straightening and molecular rearrangement of the molecules.

In order to characterize the molecular mechanism of orientation and the shape and state of the chains in the orientated polymer it is necessary to study orientation by various methods.

The anisotropy of electrical conductivity of polymeric electrolytes was investigated in the present work. Determination of the electrical conductivity of orientated and unorientated films was carried out by measurement of the current passing through the film under a chosen, applied potential. The current passing through the film between four electrodes, connected in parallel, was measured with a mirror galvanometer having a sensitivity of $1 \cdot 10^{-9}$ A.

The electrodes were fixed on an ebonite support with amber insulators at an angle of 45°, so that measurement of conductivity along and at right angles to the axis of orientation was possible by turning the support through only 90°. A special spring attached to the support enabled contact with the film to be achieved at constant pressure.

The specific conductivity was calculated by the usual equation

$$\varkappa = \frac{1}{V} \frac{l}{S}$$

where l is the length of the electrode and S is the area of cross-section of the film

* Vysokomol. soedin. **1**: No. 2, 191–200, 1959.

Assessment of the anisotropy of electrical conductivity can be made also by passing a constant current through a film lying on starch-iodine paper. By this means a coloured circle or ellipse forms, disposed differently relative to the axes, depending on the degree of orientation. The diffusion conductivity diagram made by the "trace" method on starch-iodine paper, was examined for all the orientated films.

The films were preparated from high-molecular fractions of polyacrylic and polymethacrylic acids and their salts with potassium, lithium, barium and quaternary ammonium bases, and also from mixtures of these with polyvinyl alcohol.

Polyacrylic acid was prepared by polymerization of redistilled acrylic acid in an atmosphere of nitrogen. The molecular weight of the polyacrylic acid fraction used was $(0{\cdot}5–1) \times 10^6$ and of polymethacrylic acid 80,000–100,000. In view of the fact that the presence of functional groups can exert a considerable effect on intermolecular interaction and on the rigidity of the chains in condensed systems, films from these acids diluted with polyvinyl alcohol were also investigated. The polyvinyl alcohol, of molecular weight 8,000–10,000, was purified by electrodialysis. Doubly distilled water with a specific conductivity of $1{\cdot}10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$ was used.

"Microscopical" grade glycerol, futher purified by electrodialysis, was used as plasticizer. The use of a plasticizer enabled the region of high elasticity to be extended and the films to be orientated at room temperature without lowering the breaking stress. The optimal quantity of glycerol was selected experimentally, depending on the composition of the film. For polyacrylic acid films the quantity of glycerol was 1 per cent by volume and for polymethacrylic acid, 6 per cent by volume. The films were prepared on a Terylene substrate.

The films were orientated on a Polanyi-type dynamometer, on special frames. Relaxation of the films on removal of tension served to indicate that orientation took place under a high-elasticity deformation regime and not under one of plastic flow.

RESULTS AND DISCUSSION

Values are given in Table 1 and Fig. 1 of the specific conductivity in Ω^{-1} cm^{-1} of films at various degrees of orientation (in percentages), derived from aqueous solutions of polymethacrylic acid.

In column 3 of Table 1 are shown the values of the coefficient of anisotropy of electrical conductivity i.e. the ratio of the conductivity of the film along the axis of orientation to that at right-angles to the axis.

In all the figures the continuous lines denote the values of the specific conductivity along the axis of orientation and the dotted lines that at right-angles to the axis.

Figure 2 shows the variation of the dimensionless magnitude $\varkappa/\varkappa_0$ with degree of orientation, where $\varkappa_0 = \varkappa(0)$, i.e. the value of the specific conductivity of the film at 0 per cent orientation.

TABLE 1. VALUES OF THE COEFFICIENT OF ANISOTROPY OF ELECTRICAL CONDUCTIVITY (K) FOR FILMS OF POLYELECTROLYTES AT DIFFERENT DEGREES OF ORIENTATION

Composition of film	Degree of orientation (%)	K
Polymethacrylate acid	0	0·98
	200	1·03
	300	1·09
Potassium salt of polymethacrylate acid:	0	1·04
(a) 2% neutralization	200	1·10
	300	1·20
(b) 46% neutralization	0	1·02
	200	1·12
	300	1·12
	370	1·24
(c) Polyvinyl alcohol + 1% *K* salt of polymethacrylate acid (2·2% neutralization)	0	1·1
	220	1·0
	300	1·0

Comparison of the conductivity of the orientated films along and across the axis of orientation shows that anisotropy of electrical conductivity is practically absent. The values of K, the conductivity coefficients, are close to unity for the same sample and exceed unity only within the limits of error of the experiment. Hence anisotropy is either absent or is very small.

The specific conductivity decreases with increasing orientation. For the potassium salt of polymethacrylic acid the lowering of the specific conductivity is greater the greater the degree of neutralization (curves 1 and 8).

In mixtures with polyvinyl alcohol even at a very small concentration of polymethacrylic acid (1%) and a low degree of neutralization (curve 1), marked lowering of the specific conductivity is observed on increasing the orientation.

Owing to the presence of CH_3 side chains polymethacrylic acid takes the form of extended chains even in the absence of deformation. Hence even at low degrees of orientation a decrease in electrical conductivity is observed in polymethacrylic acid films as a result of impairment of contact between bundles of chains and a decrease in their packing density.

On passing to more uncoiled types of chain—to monovalent salts of polymethacrylic and polyacrylic acids, where the molecules are even more extended by the increase in the effective charge of the chain, the decrease in electrical conductivity with orientation is even sharper (curves 1 and 8).

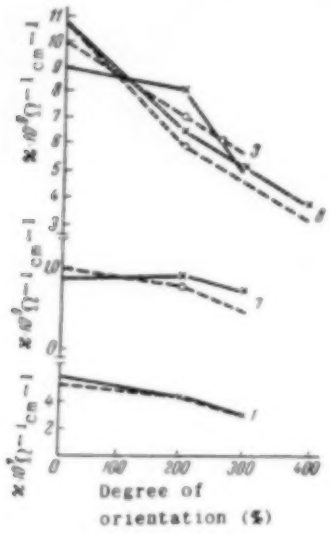

FIG. 1. Values of the specific conductivity (in Ω^{-1} cm^{-1}) for different degrees of orientation (in %) for films derived from aqueous solutions of polymethacrylic acid: 1—polyvinyl alcohol (PVA)+1% of K salt of PMA (2·2% neutralization); 3—polymethacrylic acid PMA; 7—potassium salt of PMA (2% neutralization); 8—the same (46% neutralization.).

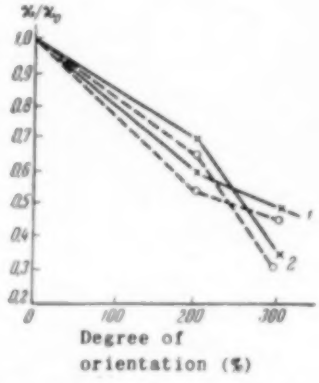

FIG. 2. Dependence of the relative specific conductivity ($\varkappa/\varkappa_0$) on the degree of orientation for polymethacrylic acid films ($\varkappa_0$ is the value of the specific conductivity at 0% orientation): 1—PVA 1% of K salt of PMA (2·2% neutralization); 2—polymethacrylic acid (PMA).

The relative lowering of the conductivity of films of polymethacrylic acid and its potassium salt, in comparison with that of unorientated films taken as unity, can be seen in Fig. 2.

Thus on orientation of films in which the polymeric electrolyte has a fibrillar structure, the value of the electrical conductivity always decreases with increasing orientation.

Values of the coefficient of anisotropy of electrical conductivity and of specific conductivity for films of polyacrylic acid are given in Table 2 and in Fig. 3 and 4.

TABLE 2. VALUES OF THE COEFFICIENT OF ANISOTROPY OF ELECTRICAL CONDUCTIVITY (K) FOR POLYELECTROLYTE FILMS AT DIFFERENT DEGREES OF ORIENTATION

Composition of film	Degree of orientation (%)	K
Polyacrylic acid	0	1·05
	200	1·04
	300	1·13
	400	1·04
	500	0·86
Potassium salt of polyacrylic acid (44% neutralization)	0	1·15
	200	0·96
	300	1·16
	500	1·00
Polyvinyl alcohol + + 1% of potassium salt of polyacrylic acid (0·5% neutralization)	0	1·0
	200	1·0
	300	0·89
Polyvinyl alcohol + + 1% of potassium salt of polyacrylic acid (64·4% neutralization)	0	1·1
	200	1·0
	300	1·0
	400	1·0

It is seen from these data that anisotropy of electrical conductivity is also not observed in films of polyacrylic acid. The change in conductivity of these films depends on the original configuration of the polyacrylic acid films.

As was shown previously [3] polyacrylic acid has a globular structure and on orientation its electrical conductivity first increases, passes through a maximum and then falls. Evidently at low degrees of orientation straightening of the polyacrylic acid chains takes place and consequently the inductivity increases. Further orientation brings about a decrease in conductivity as a result of a decrease in the continuity of structure—the appearance of microinhomogeneity.

In the case of films from salts of polyacrylic acid the decrease in conductivity is greater, the greater the degree of neutralization.

The decrease in conductivity of polyacrylic and polymethacrylic acids with orientation is evidently connected not so much with the change in packing density and the loosening of structure as with the appearance of microinhomogeneity, i.e. with the formation on orientation of bundles of chains in poor contact with one another. On altering the packing density the decrease in conductivity should be small in relation to the amount of contraction [4]; in our experiments a change in conductivity of a whole order was observed.

As is known [4] the presence of carboxyl groups causes a comparatively low specific contraction (K = 0·178 for methacrylic acid and for ethylene, for example, K = 1·14).

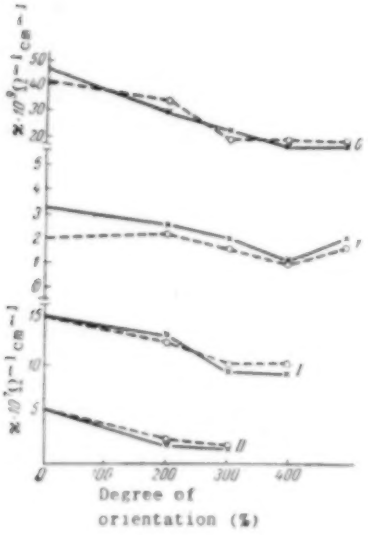

FIG. 3. Values of the specific conductivity (in Ω^{-1} cm^{-1}) at different degrees of orientation (in %) for films of polyacrylic acid: 1 – polyacrylic acid (PA); 6 – potassium salt of polyacrylic acid (44% neutralization); I – PVA 1% of K salt of PA (0·5% neutralization), II – PVA 1% of K salt of PA (64·4% neutralization).

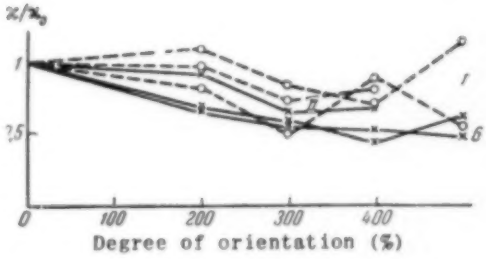

FIG. 4. Dependence of the relative specific conductivity ($\varkappa/\varkappa_0$) on the degree of orientation of polyacrylic acid (PA) films: I – polyacrylic acid (PA); 6 – potassium salt of PA (44% neutralization); II – PVA 1% of potassium salt of PA (44% neutralization).

The polymeric chains of these compounds are more rigid and pack less easily. Hence on orientation of polymeric acids the homogeneity is easily disturbed and inhomogeneity arises. In fact it has been shown by the work of Kargin and Bakeiev [3] on the structure of polyacrylic acid and its salts, by direct electron-

microscopic examination, that these systems do not give intertwining of the molecular chains but form bundles of chains and globules, i.e. they are heterogeneous systems.

The lowering of conductivity in the case of acids can be explained by the hindering of diffusion of the cations as a result of the formation of inhomogeneity on orientation.

Investigation of the electrical conductivity of films from mixtures of polyvinyl alcohol with the different acids (from 0 to 50%) and at different degrees of neutralization, for salts of monovalent cations, which give uncoiled chains — potassium, lithium and quaternary ammonium bases — confirmed the absence of anisotropy of electrical conductivity with increasing orientation.

The change in conductivity of these films is determined also by the original shape of the polymer chains.

It was of interest to investigate the dependence of electrical conductivity on degree of orientation of films of the barium salts of polyacrylic and polymethacrylic acids, which are known to have a globular configuration, in admixture with polyvinyl alcohol.

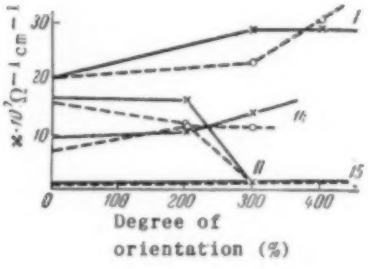

FIG. 5. Values of the specific conductivity (in Ω^{-1} cm^{-1}) at different degrees of orientation for films from mixtures of PVA with the barium salts of polyacrylic and polymethacrylic acids: I—PVA 1% of PA Ba″ (33% neutralization); II— PVA 1% of PA Ba″ (83% neutralization); 14—PVA 1% of PMA Ba″ (50% neutralization); 15—PVA 20% PMA Ba″ (50% neutralization).

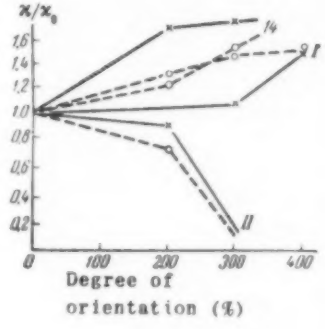

FIG. 6. Dependence of the relative specific conductivity ($\varkappa/\varkappa_0$) on the degree of orientation of films from mixtures of PVA with the barium salts of polyacrylic and polymethacrylic acids: 1—PVA 1% PA Ba″ (33% neutralization); II—PVA 1% PA Ba″ (83% neutralization); 14—PVA 1% PMA Ba″ (50% neutralization).

The barium salts give conglomerates with a less diffuse structure in comparison with polyacrylic acid, because here in addition to thermal forces there are larger intermolecular forces resulting from the interaction of divalent barium

with the carboxyl groups. In the process of orientation extension of the chains takes place, which leads to an increase in conductivity on deformation. The greater the degree of neutralization the more stable are the globules and extension of the chains is more difficult.

On Fig. 5 and 6, and in Table 3 are shown the coefficients of anisotropy of electrical conductivity and the specific conductivities of films from mixtures of the barium salts of polyacrylic and polymethacrylic acids with polyvinyl alcohol at different degrees of orientation.

TABLE 3. VALUES OF THE COEFFICIENT OF ELECTRICAL CONDUCTIVITY (K) OF POLYELECTROLYTE FILMS AT DIFFERENT DEGREES OF ORIENTATION

Composition of film	Degree of orientation (%)	K
Polyvinyl alcohol + + 20% of barium polymethacrylate (50% neutralization)	0	0·90
	300	1·0
	400	1·0
Polyvinyl alcohol + + 1% of barium polymethacrylate (33% neutralization)	0	0·99
	200	1·0
	300	1·1
	400	0·98
Polyvinyl alcohol + + 1% of barium polymethacrylate (83% neutralization)	0	1·0
	300	1·0
	400	0·99
Polyvinyl alcohol + + 1% of barium polymethacrylate (50% neutralization)	0	0·88
	300	1·0
	400	1·0

The barium salt of polyacrylic acid, even at a low salt content, in the mixtures with polyvinyl alcohol, shows an increase in conductivity in the case where the globules were less stable (curve I—degree of neutralization 33%). In the case of almost complete neutralization (curve II—83% neutralization) the globules are more stable, but a small degree of orientation, sufficient to reduce the contact between them, again brought about a decrease in conductivity.

With the barium salt of polymethacrylic acid at the same degree of neutralization (50%) the greatest increase in conductivity is observed where the salt content in the polyvinyl alcohol mixture is least. The change in conductivity shows up less in the case of the barium salt of polymethacrylic acid because the latter itself has an extended configuration.

Anisotropy of electrical conductivity is again not observed in films from the barium salts of these acids.

Double Refraction. The appearance of anisotropy on orientation of flexible, chain molecules is connected not only with straightening of the whole molecule but also with extension of its microsegments. Different methods of assessment of orientation enable conclusions to be drawn about the orientation, about the shape and state of the chains in the orientated polymer, and also about the flexibility of the chains. Consequently in parallel with the determination of electrical conductivity control experiments were run on the occurrence of anisotropy with increase in orientation, by other methods also, i.e. optically, by X-ray analysis and from conductivity diffusion diagrams.

In all the films examined optical anisotropy was observed, i.e. an increase in the angle of double refraction with increasing orientation. This is illustrated by Tables 4 and 5 and Fig. 7 and 8 which show the dependence of double refraction on orientation for films of the potassium and barium salts of polymethacrylic acids.

TABLE 4. DEPENDENCE OF DOUBLE REFRACTION ON DEGREE OF ORIENTATION

Composition of film	Degree of orientation (%)	Double refraction
Polyvinyl alcohol + + 10% of potassium salt of polymethacrylic acid (60·6% neutralization)	0	0
	200	$1{\cdot}6\times10^{-3}$
	300	$3{\cdot}2\times10^{-3}$
	400	$5{\cdot}5\times10^{-3}$

The conductivity diffusion diagram always gave an undistorted picture in the form of a circle, as is seen from Fig. 9.

The X-ray diffraction patterns of polyacrylic and polymethacrylic acids at various degrees of orientation were vague and diffuse. Texture appears in the case of films from mixtures of polyvinyl alcohol with the potassium and barium salts (Fig. 10, 11 and 12) at degrees of orientation of 400 and 500%.

TABLE 5. DEPENDENCE OF DOUBLE REFRACTION ON DEGREE OF ORIENTATION OF POLYELECTROLYTE FILMS

Composition of film	Degree of orientation (%)	Double refraction
Polyvinyl alcohol + + 20% of barium salt of polymethacrylate acid (33% neutralization)	0	0
	200	$0{\cdot}076 \times 10^{-3}$
	300	$0{\cdot}13 \times 10^{-3}$

For comparison a crystalline film of a technical polyamide was examined, because this also does not show anisotropy of electrical conductivity at degrees of orientation from 0 to 500%.

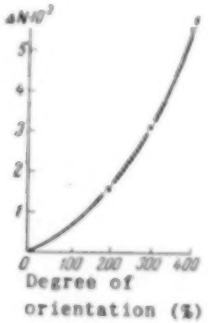

FIG. 7. Dependence of double refraction on degree of orientation for films from a mixture of polyvinyl alcohol (PVA) and 10% of the potassium salt of polymethacrylic acid (60·6% neutralization).

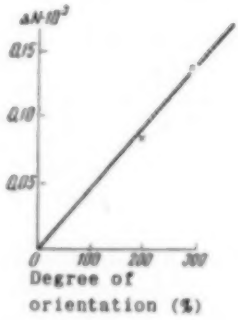

FIG. 8. Dependence of double refraction on degree of orientation for films from a mixture of polyvinyl alcohol and 20% of the barium salt of polymethacrylic acid (33% neutralization).

A decrease in conductivity with increasing orientation was observed with this film, which is known [1] to be connected with disordering of the crystalline polymer on deformation.

Hence our investigation has shown that the decrease in conductivity of bundles of extended chains is connected with disordering of the system, with the appearance of microinhomogeneity. Evidently we observe a decrease in

conductivity in those cases where the relaxation rate is small in comparison with the time scale of the experiment.

This hypothesis is confirmed by experiments on the effect of thermal relaxation on the change in conductivity of the films. Samples of orientated film, covered with foil or polyethylene film were firmly clamped between two glass plates and heated at T =100° for 15–20 hr. The samples were then either chilled rapidly or cooled slowly (at the rate of 10° per hr).

It was found that on chilling, the packing density was somewhat lower than that found where there is orientation.

We observed first an increase in conductivity and then subsequently a decrease. On slow cooling the thermal-relaxation processes take place at a high rate. Under these conditions the packing density correspondingly increases and the lowering in conductivity decreases.

Thermal relaxation did not show a significant effect on the change in conductivity because the decrease in conductivity, connected with extension of the chains, is here lower than on orientation of the polymer.

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CONCLUSIONS

(1) Investigation has shown that orientated films of polyelectrolytes (polyacrylic and polymethacrylic acids and their salts) do not display anisotropy of electrical conductivity. On orientation of flexible molecules under conditions of high-elastic deformation, relative extension of only large chain segments takes place, orientation of this order (up to 500%) does not affect small segments of the chains. Because anisotropy of electrical conductivity can be detected only on extension of small chain segments, flexible chain systems do not show this phenomenon. Evidently, on orientation a significant change in the distance between the ionizable groups both within and between the chains does not take place, and this is connected with the flexibility of the chains. The absence of anisotropy of electrical conductivity indicates that there is no preferential conductivity with respect to the chains of a polyelectrolyte. The absence of anisotropy is connected with the absence of macrodefects in the film and provides a good indication of its quality.

(2) The nature of the changes in electrical conductivity that take place with increasing orientation in polymeric films is determined by two types of polyelectrolyte structure, globular formations and bundles of extended chains. Correspondingly the occurrence of two types of change in conductivity with increasing orientation was observed:

(a) a decrease in conductivity, when the molecules are extended (in the case of polymethacrylic acid and its salts with monovalent cations), which can be explained by hindering of the diffusion of the cations as a result of the formation of inhomogeneity on orientation;

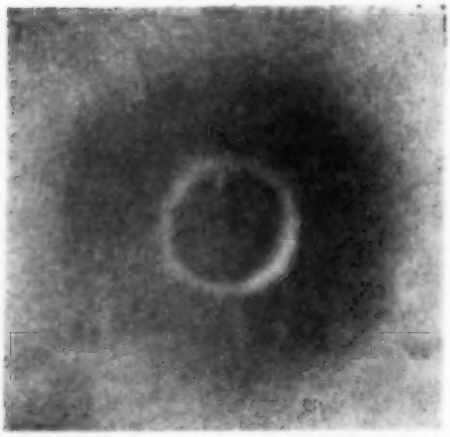

FIG. 9. Conductivity diffusion diagram (by the "trace" method on starchiodine paper)

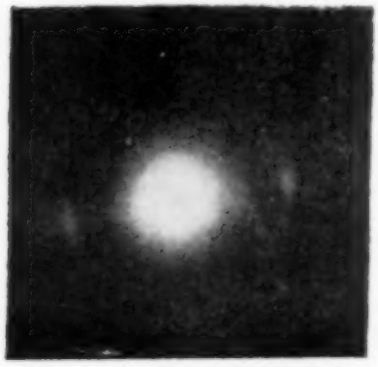

FIG. 10. Polyvinyl alcohol 20% PMA K. (60·6% neutralization); orientation 300%.

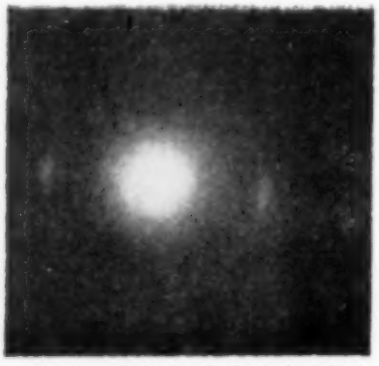

FIG. 11. Polyvinyl alcohol 50% PMA Ba" (50% neutralization); orientation 400%.

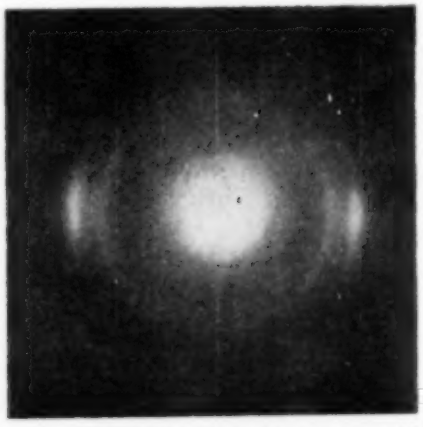

FIG. 12. Polyamide film; orientation 500%.

(b) an increase in conductivity, observed in the case of globular structures where orientation assists uncoiling of the globules (in the case of the barium salts of polyacrylic and polymethacrylic acids);

(c) an intermediate case, an increase in conductivity and a subsequent decrease occurs in cases where the globules are unstable, and twist and uncoil easily (polyacrylic acid).

In the limit, for large deformations, a decrease in conductivity is always characteristic of polyelectrolytes. The physical significance of this change in conductivity with orientation consists in the fact that deformation brings about a disordering of the system of chains. Hence if the rate of relaxation is small in comparison with the time scale of the experiment we observe a decrease in conductivity. Consequently the nature of the change in conductivity is not simply connected with the degree of orientation but depends on the histroy of the polyelectrolyte, i.e. on the initial shape of its macromolecules.

(3) A change in electrical conductivity with orientation should not be observed where there are chaotically entangled chains. The change is in fact connected with the existence of bundles of chains or globules, the contact between which is impaired as orientation increases.

(4) The cause of the change in conductivity that takes place on orientation is not the mean change in density, connected with uncoiling of the structure and the change in packing density, but the appearance of microinhomogeneity, i.e. the formation on orientation of bundles of chains in poor contact with one another. If only the packing density were disturbed the decrease in conductivity would be small, corresponding to the amount of contraction ; in our case a change in conductivity of a whole order was observed.

The occurrence of microinhomogeneity, which was observed directly in the electron microscope, confirms the hypothesis concerning the inhomogeneity of "secondary structures" of the polymeric electrolyte macromolecules.

Translated by E. O. PHILLIPS

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HETEROCHAIN POLYAMIDES: SYNTHESIS AND INVESTIGATION OF POLYAMIDES CONTAINING SULPHIDE AND SULPHONIC SULPHUR IN THE CHAIN*

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(*Received* 10 *July* 1957)

THERE is a fairly considerable amount of patent literature on the synthesis of polyamides containing sulphur and oxygen links and a few papers mention the synthesis and properties of such polyamides. Polyamides containing oxygen and sulphur are usully hydrophilic; products from such polyamides dye considerably more easily and more uniformly than polyamides which do not contain oxygen and sulphur. The synthesis of such polyamides was brought about by polycondensation of dicarboxylic acids containing sulphur or ether links, with diamines. Dicarboxylic acids of this type, which contain sulphide and sulphonic sulphur, include dithioglycollic [1], thiodibutyric [2], thiodipropionic and its sulphone [2, 3], bis(4-carboxy-benzene)-sulphide [2] and a number of others [4].

In this paper an account is given of the results of synthesis and investigation of polyamides from thiodivaleric, sulphonyldivaleric and thiodioenanthic acids with hexamethylenediamine and ethylenediamine. The above acids were kindly presented to us by Freidlina [5]. For the synthesis of the polyamides we used the salts of the acids with the diamines. It should be noted that in order to obtain salts of good quality it is necessary to use very pure initial acids and diamines, otherwise it is impossible to purify the salts even by multiple recrystallization.

Synthesis of the polyamide from thiodivaleric acid and hexamethylenediamine (I): From thiodivaleric acid and hexamethylenediamine polyamides of specific viscosity from 0·2–1·48 (0·5% solution in m-cresol) were obtained. These polyamides were solid, somewhat coloured resins, melting at ~ 180°, soluble in phenols, mineral acids, formic acid and hot acetic acid. At a sufficiently high molecular weight they acquire the ability to be drawn out into filaments from the melt. The filaments are very elastic and can be cold drawn. The polyamides are less heat stable than polymexamethylenediamide. Thus, on carrying out the reaction at 260° a decrease in molecular weight begins after 4–5 hr.

* Vysokomol. soedin. **1**: No. 2, 208–214, 1959.

Synthesis of the polyamide from sulphonyldivaleric acid and hexamethylenediamine (II): A polyamide of the structure — $CO(CH_2)_4SO_2(CH_2)_4CONH(CH_2)_6NH$ — was prepared by two methods:

(1) by polycondensation of the salt of sulphonylvaleric acid with hexamethylenediamine;

(2) by oxidation of the polyamide (I) with hydrogen peroxide.

In the first case a polyamide having a maximum specific viscosity of 0·730 was obtained. It is a solid, slightly coloured resin, melting at about 215° and possessing fibre-forming properties. Its heat stability was a little lower than that of I.

On oxidation of I with hydrogen peroxide in formic acid a polyamide containing sulphonic sulphur was obtained having a maximum specific viscosity of 1·15. Analysis of the oxidized polyamide showed that all the sulphide sulphur had been oxidized to sulphonyl sulphur. The oxidized polyamide had the same melting point as that of the polyamide II.

We attempted to make a polyamide from the sulphoxide of thiodivaleric acid and hexamethylenediamine but this was unsuccessful because decomposition of the salt of this sulphoxide with hexamethylenediamine takes place below its melting point.

Synthesis of the polyamide from thiodioenanthic acid and hexamethylenediamine (III): On preparing this polyamide by heating the salt of thiodioenanthic acid and hexamethylenediamine under approximately the conditions as in the synthesis of (I) the product had a maximum specific viscosity of 1·10 and a melting point of ~ 170°. As in the first two cases the polymer was a solid, slightly coloured resin, possessing fibre-forming properties.

Synthesis of polyamides from ethylenediamine and thiodicarboxylic acids. The synthesis of polyamides from ethylenediamine should be of considerable interest because on the one hand such polyamides should have a higher melting point than those based on hexamethylenediamine, and on the other hand their production should be favoured by the cheapness and availability of ethylenediamine. Attempts to prepare polyamides from ethylenediamine and dicarboxylic acids are described in the literature. Thus, Korshak and Rafikov [6] have published data on the preparation of polyamides from ethylenediamine and adipic and sebacic acids. Like previous investigators [7], they did not succeed in obtaining a high-molecular polyamide from ethylenediamine and adipic acid, and they explained this by the tendency of these materials to form cyclic polycondensation products. From ethylenediamine and sebacic acid they obtained a polyamide having a specific viscosity of 0·230.

We prepared polyamides from ethylenediamine and thiodivaleric and thiodioenanthic acids. As in the previous cases the salts of the acids with ethylenediamine were condensed. A polyamide having a maximum specific viscosity of 0·37 and m.p. ~ 220° was obtained from the diamine and thiodivaleric acid. From ethylenediamine and thiodioenanthic acid a polyamide was obtained

having a maximum specific viscosity of 0·38 and m.p. ~ 210°. We did not succeed in preparing polyamides of higher molecular weight even on carrying out a second reaction stage under high vacuum. In external form these polyamides are like that from thiodivaleric acid and hexamethylenediamine but they are rather brittle and do not form fibres. This is evidently connected with their low molecular weight.

EXPERIMENTAL

Preparation of the salt of thiodivaleric acid and hexamethylenediamine. 1 g-mole of thiodivaleric acid (m.p. 94–94·5) was dissolved by heating in 700 ml of ethyl alcohol (complete solution was not always obtained) and a solution of 1·05–1·1

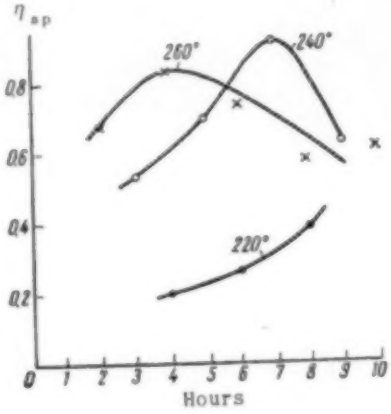

FIG. 1.

g-moles of freshly distilled hexamethylenediamine in of 60–100 ml of ethyl alcohol was added to the hot solution (or mixture) with stirring. The resulting clear solution was filtered. White crystals of the salt precipitated from the solution on cooling. Yield, 80 per cent m.p. 167–169°. After 1–2 recrystallizations from aqueous alcohol it had m.p. 170–171°.

	Found % :	S 8·83 ; 8·85 ; N 8·12 ; 8·29.
$C_{10}H_{24}O_4N_2S$.	Calculated % :	S 9·14 ; N 8·00.

Synthesis of the polyamide from thiodivaleric acid and hexamethylenediamine. (I). The polyamide was prepared as described previously [8], by heating the above salt in condensation tubes in an atmosphere of nitrogen. Before the commencement of heating the air in the tube containing the salt was thoroughly swept out by nitrogen. During the first hour the temperature of the bath was maintained at 170–180°, and during the second hour at 190° after which the temperature was raised rapidly to a chosen point and held for the required time. The reaction

conditions and the specific viscosities of 0·5% solutions in m-cresol of the polyamides obtained are indicated in Table 1 and in the diagram. In order to obtain polyamides of higher molecular weight the reaction was carried out as follows: in the first stage of the reaction the salt was heated in sealed ampoules (the ampoules were first successively evacuated and filled with nitrogen a few times)

TABLE 1. SYNTHESIS OF THE POLYAMIDE FROM THIODIVALERIC ACID AND HEXAMETHYLENEDIAMINE

Reaction No.	2nd reaction stage		Specific * viscosity, η_{sp}	Reaction No.	2nd reaction stage		Specific * viscosity, η_{sp}
	Temperature (°C)	Time (hr)			Temperature (°C)	Time (hr)	
1	200	4	0·205	7	240	9	0·630
2	200	6	0·256	8	260	2	0·688
3	200	8	0·389	9	260	4	0·840
4	240	3	0·535	10	260	6	0·743
5	240	5	0·690	11	260	8	0·583
6	240	7	0·920	12	260	10	0·635

* Mean of two determinations.

at 180–190° for 3–6 hr. Heating was then continued for 3–5 hr at 220° in a current of nitrogen and finally for 2–3 hr *in vacuo* at 220–240°. Data on these reactions are shown in Table 2.

TABLE 2. SYNTHESIS OF THE POLYAMIDE FROM THIODIVALERIC ACID AND HAEMETHYLENEDIAMINE

Reaction No.	Time of heating (hr)				Specific* viscosity, η_{sp}
	in ampoules at 180–190°C	in current of nitrogen at 220°C	in vacuum, 1–2 mm at 220°C	in high vacuum	
13	3	3	3	–	1·19
14	6	3	3	–	1·14
15	6	3	2	3	1·478
16	4	5	3	–	1·146

* Mean of two determinations.

Preparation of the salt of sulphonyldivaleric acid and hexamethylenediamine. The salt was prepared as in the previous case but 70% aqueous alcohol was used; yield 75%; m.p. 182–183°.

Found %: S 8·46; 8·44; N 7·26; 7·16.

$C_{16}H_{34}O_6N_2S$. Calculated %: S 8·37; N 7·33.

Synthesis of the polyamide from sulphonyldivaleric acid and hexamethylenediamine. (II) This polyamide was prepared in the same way as that from thiodivaleric acid and hexamethylenediamine. The salt was heated at 180–200° for the first hour and then for 2–8 hr at the chosen temperature. The reaction conditions and the specific viscosity of 0·5% solutions in m-cresol of the polyamides obtained are given in Table 3.

TABLE 3. SYNTHESIS OF THE POLYAMIDE FROM SULPHONYLDIVALERIC ACID AND HEXAMETHYLENEDIAMINE

Reaction No.	2nd reaction stage		Specific viscosity, η_{sp}	Reaction No.	2nd reaction stage		Specific viscosity, η_{sp}
	Temperature (°C)	Time (hr)			Temperature (°C)	Time (hr)	
17	230	3	0·358	23	240	6·5	0·410
18	230	4	0·557	24	240	7·5	0·50
19	230	5	0·353	25	260	2	0·50
20	240	2	0·735	26	260	5·5	0·467
21	240	4	0·720	27	260	7	0·350
22	240	5·5	0·490	28	260	8·5	0·320

Oxidation of the polyamide (I) [9]. 2 g of the finely ground polyamide was dissolved in 25 ml of formic acid (85%), with stirring and slight heating (to 30–40°) for a few hours. The resulting solution was cooled in ice and 3·6 g of 30% hydrogen peroxide was added to the cold solution slowly, to prevent heating up. The solution was allowed to stand at room temperature for 3–4 hr and it was then poured slowly into a large volume of distilled water, with continuous stirring.

TABLE 4. OXIDATION OF THE POLYAMIDE FROM THIODIVALERIC ACID AND HEXAMETHYLENEDIAMINE

Reaction No.	Specific viscosity η_{sp}	Found %				Calculated %			
		C	H	S	N	C	H	S	N
29 original	1·350								
29 oxidized	1·166	—	—	—	—	—	—	—	—
30 original	0·879	60·70	9·69	10·03	8·49	61·2	9·56	10·2	8·91
		60·61	9·70	10·03	8·74				—
30 oxidized*	0·653	—	—	—	—	—	—	—	
30 oxidized	0·770	54·9	8·91	8·75	7·39	55·5	8·68	9·25	8·10
		54·9	9·08	8·82	7·55				

* During oxidation the temperature of the solution fell to that of the room.

The fibrous precipitate of polymer was filtered off, washed very thoroughly on the filter with water and then acetone, and dried in air. Yield 2·1 g; m.p. ~215°. Data on the oxidation are given in Table 4.

Preparation of the salt of thiodioenanthic acid and hexamethylenediamine. The salt was prepared as in the previous cases but in anhydrous ethanol. The salt was obtained in two modifications: anhydrous, m.p. 115–116°, and containing alcohol of crystallization, m.p. 151–152°.

Found %: C 58·86; 58·91; H 10·42; 10·51; S 7·92; 7·75.
$C_{20}H_{42}O_4N_2S$. Calculated %: C 59·91; H 10·34; S 7·88.

Synthesis of the polyamide from thiodioenanthic acid and hexamethylenediamine. (III) Condensation of the salt was carried out in the usual manner, the first stage of the reaction was carried out both in ampoules and in a current of nitrogen. The final stage was conducted *in vacuo*. The experimental results are given in Table 5.

TABLE 5. SYNTHESIS OF THE POLYAMIDE FROM THIODIOENANTHIC ACID AND HEXAMETHYLENEDIAMINE

Reaction No.	2nd stage of reaction		Other reaction conditions	Specific viscosity η_{sp}
	Time (hr)	Temperature (°C)		
31	1	180	Current of nitrogen	0·770
	4	180	Vacuum	
32	1	185	,,	0·950
	6	185		
33	1	188	,,	0·70
	8	188		
34	1	190	,,	0·75
	7	190		
35	1	200	,,	0·80
	6	200		
36	1	200	,,	0·222
	6	210		
37	1	220	,,	0·840
	4	220		

Note: The first stage of the reaction was carried out in an ampoule at 180°C for 5 hr.

Preparation of the salt of thiodivaleric acid and ethylenediamine. 75–78% aqueous ethylenediamine was used in the preparation of the salt. 20 g of the acid was dissolved by heating in 150 ml of ethanol and 7·4 g of aqueous ethylenediamine (10% excess) was added to the hot solution. The salt precipitated on standing and cooling. Yield 23 g (91% of theory). After recrystallization from ethanol, m.p. 134–134·5°.

Found %: C 49·08; 49·31; H 8·91; S 11·08; 11·05.
$C_{12}H_{26}O_4N_2S$. Calculated %: C 48·98; H 8·85; S 10·90.

Synthesis of the polyamide from thiodivaleric acid and ethylenediamine. Condensation of the salt was carried out in the usual manner. The first stage was carried out in ampoules or in a current of nitrogen, and the final stage *in vacuo* (including high vacuum). The results of some reactions are given in Table 6.

TABLE 6. SYNTHESIS OF THE POLYAMIDE FROM THIODIVALERIC ACID AND ETHYLENEDIAMINE

Reaction No.	2nd stage of reaction		Other reactions	Specific viscosity η_{sp}
	Time (hr)	Temperature (°C)		
38	1	218	Current of nitrogen	0·34
	4	218	Vacuum	
39	1	230	,,	0·30
	4	230		
40	2	230	,,	0·33
	6	230		
41	2	230	,,	0·31
	8	230		
42	2	230	,,	0·37
	10	230	,,	
43	1	240	,,	0·37
	4	240		

Note: The first stage of the reaction was carried out in ampoules.

TABLE 7. SYNTHESIS OF THE POLYAMIDE FROM THIODIOENANTHIC ACID AND ETHYLENEDIAMINE

Reaction No.	2nd stage of reaction		Other reaction conditions	Specific viscosity η_{sp}
	Time (hr)	Temperature (°C)		
44	4	245	Current of nitrogen	0·33
45	8	245	,,	0·275
46	2	265	,,	0·235
47	4	265	,,	0·270
48	2	250	,,	
	2	250	Vacuum, 2mm	0·335
49	2	250	Current of nitrogen	
	4	250	Vacuum, 2mm	0·370
50	2	250	Current of nitrogen	
	6	250	Vacuum, 2mm	
	3	250	Vacuum 1×10^{-5}mm	0·370
51	2	250	Current of nitrogen	
	6	250	Vacuum 1×10^{-2}mm	
	4	250	Vacuum 1×10^{-5}mm	0·30

* The first stage of the reaction was carried out in ampoules.

Preparation of the salt of thiodioenanthic acid and ethylenediamine. The salt was prepared in the same way as in the previous cases, yield 60%, m.p. 142–143°.

Found %: C 54·81; 54·75; H 9·56; 9·68; S 9·16; 9·18.
$C_{20}H_{42}O_4N_2S$. Calculated %: C 54·90; H 9·53; S 9·15.

Synthesis of the polyamide from thiodioenanthic acid and ethylenediamine. Condensation of the salt was carried out as in the previous cases. The results of the some reactions are given in Table 7.

CONCLUSIONS

Polyamides from hexamethylenediamine and the following dicarboxylic acids have been synthesized: thiodivaleric (m.p. of amide ~ 180°); sulphonyldivaleric (m.p. ~ 215°) and thiodioenanthic (m.p. ~ 170°). All the polyamides synthesized possessed fibre-forming properties.

Translated by E. O. PHILLIPS

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THE ACTION OF BINARY SYSTEMS OF VULCANIZATION ACCELERATORS *

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(*Received* 8 *January* 1919)

MIXTURES of two or more accelerators, as a rule, have a higher vulcanization activity than each of the given accelerators used singly. In spite of the wide practical application of combinations of accelerators the mechanism of their simultaneous action has not been studied sufficiently. For example, the principles of composition of binary and ternary accelerator systems have not yet been established.

Usually the increase in vulcanization activity under the action of two accelerators is regarded as the result of the formation of salt-type complexes between the two [1, 2, 3], which are more powerful accelerators than the original compounds.

The present communication describes the results of an investigation of a number of double vulcanization-accelerator systems, differing in chemical structure:

(a) Organic disulphides and nitrogenous organic bases (di-2-benzothiazyl disulphide–diphenylguanidine, di-2-benzothiazyl disulphide–hexamethylenetetramine, tetramethylthiuram disulphide–diphenylguanidine, tetramethylthiuram disulphide–hexamethylenetetramine).

(b) Organic disulphides and sulphenamides (di-2-benzothiazyl disulphide–N,N–diethyl-2-benzothiazolsulphenamide, di-2-benzothiazyl disulphide–N-cyclohexyl-benzothiazylsulphenamide, tetramethylthiuram disulphide–N-cyclohexyl-benzothiazol-sulphenamide.

(c) Sulphenamides and nitrogenous organic bases (N-cyclohexyl-2-benzothiazolsulphenamide–diphenylguanidine, N,N-diethyl-2-benzothiazolsulphenamide–diphenylguanide, N-cyclohexyl-2-benzothiazolsulphenamide–hexamethylenetetramine, N,N-diethyl-2- benzothiazolsulphenamide–hexamethylenetetramine.

(d) Mercaptans and nitrogenous organic bases — 2-mercapto-benzothiazol in combination with diphenylguanidine, hexamethylenetetramine and melamine.

(e) Sulphenamides (N-cyclohexyl-2-benzothiazolsulphenamide and N,N-diethyl-2-benzothiazolsulphenamide) and also disulphides (di-2-benzothiazyl disulphide) in combination with tetramethylthiuram monosulphide.

* Vysokomol. soedin. **1**: No. 2, 254–264, 1959.

As is seen from the above list, a very wide range of vulcanization accelerators was chosen for investigation.

The dynamics of vulcanization of butadiene-styrene rubber in the presence of the above combinations of accelerators was studied in mixtures of the following composition: SKS-30AM rubber—100·0 parts by weight, stearic acid—2·0, accelerators—in various proportions, zinc oxide—5·0, Channel black—30·0 and sulphur—2·0. In all cases the thermoplastic rubber SKS-30AM having a Karrer plasticity of 0·50–0·55, was used.

The dynamics of vulcanization of the rubber mixtures was investigated by studying the change in their physicomechanical properties, the quantity of sulphur combined with the resin, and the change in the degree of swelling.

In addition to this experiments were carried out to determine the nature of some of the accelerators with one another in a solvent medium and in the presence of the rubber.

THE DYNAMICS OF VULCANIZATION OF RUBBER MIXTURES

Disulphides and nitrogenous organic bases. The systems di-2-benzothiazyl disulphide–diphenylguanidine, di-2-benzothiazyl disulphide–hexamethylenetetra-

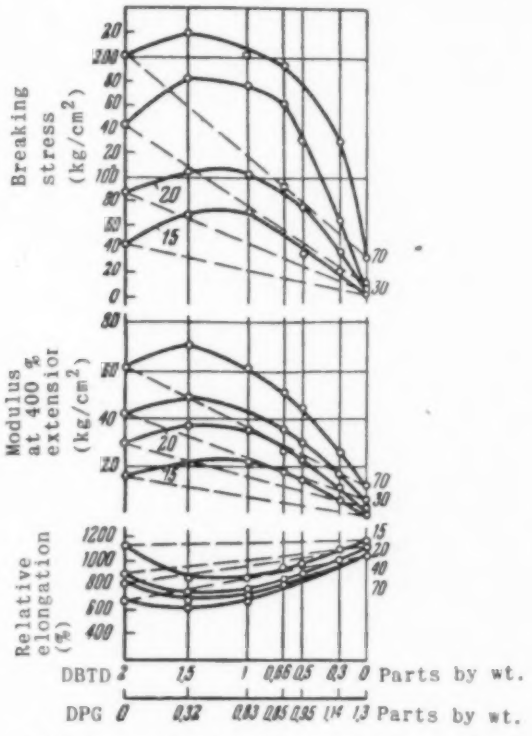

Breaking stress (kg/cm²)
Modulus at 400 % extension (kg/cm²)
Relative elongation (%)
DBTD 2 1,5 1 0,66 0,5 0,3 0 Parts by wt.
DPG 0 0,32 0,83 0,85 0,95 1,14 1,3 Parts by wt.

FIG. 1. Activity of the binary system di-2-benzothiazyl-disulphide–diphenylguanidine.

mine and tetranethylthiuram disulphide–hexamethylenetetramine show a well defined mutual activation of the accelerators.

Figure 1 shows the change in physicomechanical properties of the rubber mixtures containing the di-2-benzothiazyl disulphide–diphenylguanidine system. The figures on the abscissa indicate that though the proportions of the accelerators were varied the total molar concentration was kept constant. The straight, dotted lines on this and subsequent digrams, which join the indices of vulcanization activity of each accelerator used alone, indicate approximately the change in properties that would correspond to the additive effect of the accelerators.

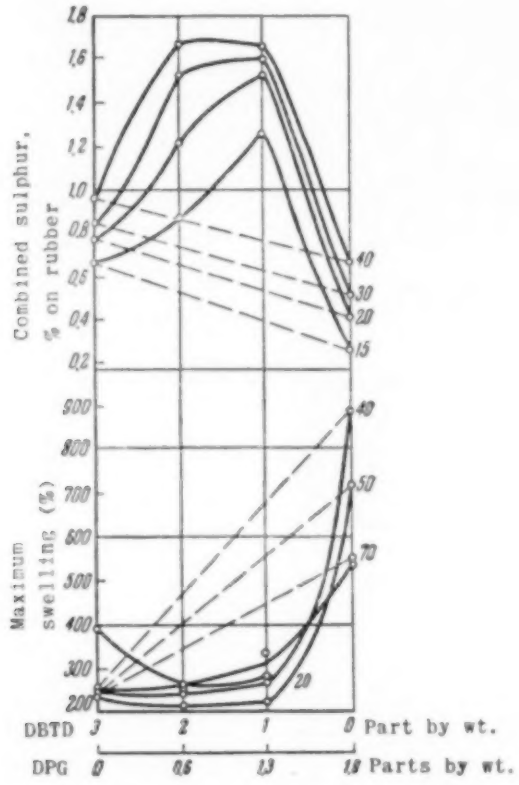


FIG. 2. Variation in combined-sulphur content and maximum swelling of the mixtures in the presence of di-2-benzothiazyldisulphide and diphenylguanidine.

The data given in Figure 1 (the numbers on the curves denote the vulcanization time in minutes) indicate that for this system the activity of the accelerators is not additive. For all ratios of di-2-benzothiazyl-disulphide : diphenyl-guanidine there are higher values for the tensile strength and modulus of the mixture, a larger amount of combined sulphur and a lower maximum swelling (Fig. 2) than for the two accelerators used separately. A similar activity is characteristic also of the other accelerators of this class, examined.

Disulphides and sulphenamides. All three accelerator systems tested, di-2-benzothiazyl disulphide–N,N-diethyl-2-benzothiazolsulphenamide, di-2-benzothiathiazyl disulphide–N-cyclohexyl-2-benzothiazolsulphenamide and tetramethylthiuram disulphide–N-cyclohexyl-2-benzothiazolsulphenamide, displayed considerable mutual activity shown by increased tensile strength and modulus in comparison with vulcanizate mixtures containing these accelerators taken single.

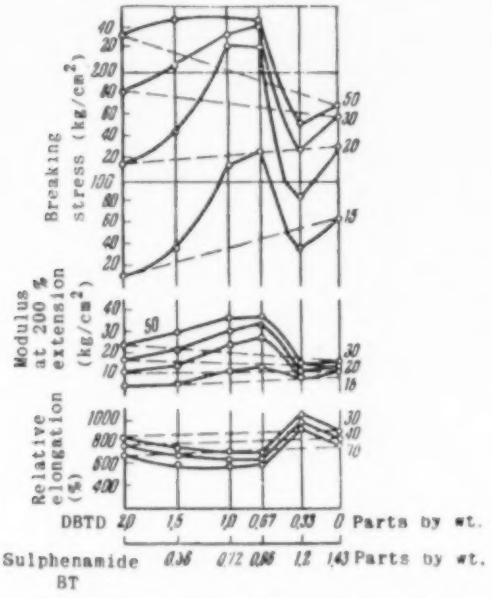

Breaking stress (kg/cm²)
Modulus at 200 % extension (kg/cm²)
Relative elongation (%)
DBTD 2,0 1,5 1,0 0,67 0,33 0 Parts by wt.
Sulphenamide BT 0,36 0,72 0,86 1,2 1,43 Parts by wt.

FIG. 3. Activity of the binary system di-2-benzothiazyl-disulphide–N,N-diethyl-2-benzothiazolsulphenamide.

The system di-2-benzothiazyl disulphide–N-cyclohexyl-2-benzothiazolsulphenamide behaves similarly to the di-2-benzothiazyl disulphide–N,N-diethyl-2-benzothiazolsulphenamide system (Fig. 3). In these cases the maximal accelerator activity occurs at a ratio close to equimolar. It is interesting to note that in the latter system at a ratio of 0·33 parts by weight of the disulphide to 1·2 parts of the sulphenamide, vulcanization is retarded, as indicated by a decrease in tensile strength and modulus.

The results obtained on the kinetics of vulcanization of rubber mixtures containing di-2-benzothiazyl disulphide and N,N-diethyl-2-benzothiazolsulphenamide confirm the earlier observation [4] that vulcanization is retarded in the initial period with the system tetramethylthiuram disulphide–di-2-benzothiazyl disulphide. As the results show, with respect to combination of sulphur in the early stages of vulcanization of butadiene-styrene rubber mixtures, filled with channel black (Fig. 4, curve corresponding to 5 minutes), the system of two accelerators has a lower vulcanizing effect than each of the corresponding accel-

erators used separately. In the later stages of vulcanization (after 10 min) an increase in the vulcanization activity occurs, as is seen from the data on the

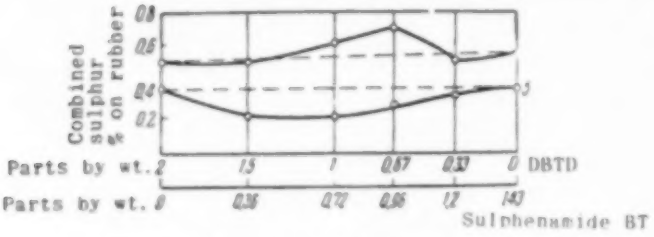


FIG. 4. Variation in combined-sulphur content on vulcanization in the presence of di-2-benzothiazyldisulphide and N,N-diethyl-2-benzothiazolsulphenamide.

change in physicomechanical properties of the vulcanizates (Fig. 3). Retardation of vulcanization during the first 5–10 min is quite marked in the case of vulcanization of unfilled mixtures also (Fig. 5).

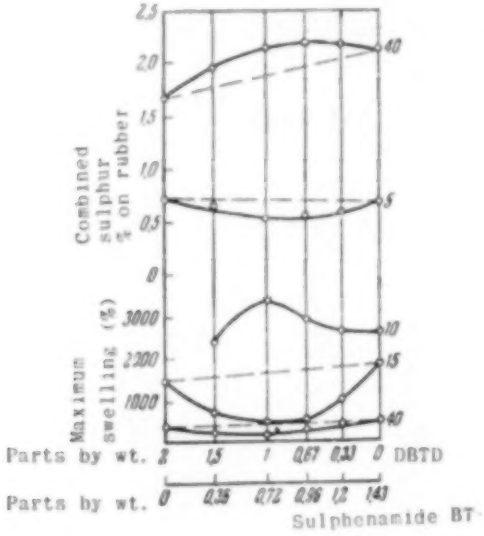


FIG. 5. Variation in combined-sulphur content and maximum swelling of unfilled mixtures on vulcanization in the presence of di-2-benzothiazyldisulphide and N,N-diethyl-2-diethyl-2-benzothiazylsulphenamide.

Sulphenamides and nitrogenous organic bases. The results indicated in Figure 6 characterize the activity of accelerator combinations of this class, in the vulcanization of rubber mixtures, in particular for the system N-cyclohexyl-2-benzolsulphenamide–diphenylguanidine. In mixtures containing N-cyclohexyl-2-benzothiazolsulphenamide, diphenylguanidine lowers the breaking stress and

modulus in comparison with mixtures containing this sulphenamide alone. The activities of the accelerators of this system are not additive. In this case mutual activation of the accelerators does not occur, only activation of one of them takes place, i.e. that of diphenylguanidine by the sulphenamide. The breaking stress and modulus of mixtures containing these two accelerators in combination are a little higher than the values obtained with diphenylguanidine alone but they are not greater than, and in a number of cases do not reach, the tensile-strength and modulus values of mixtures containing only the sulphenamide. The data on the kinetics of combination of sulphur (Fig. 7) confirm the conclusion that for these systems activation of one of the accelerators occurs, that belonging to the class of nitrogenous organic bases.

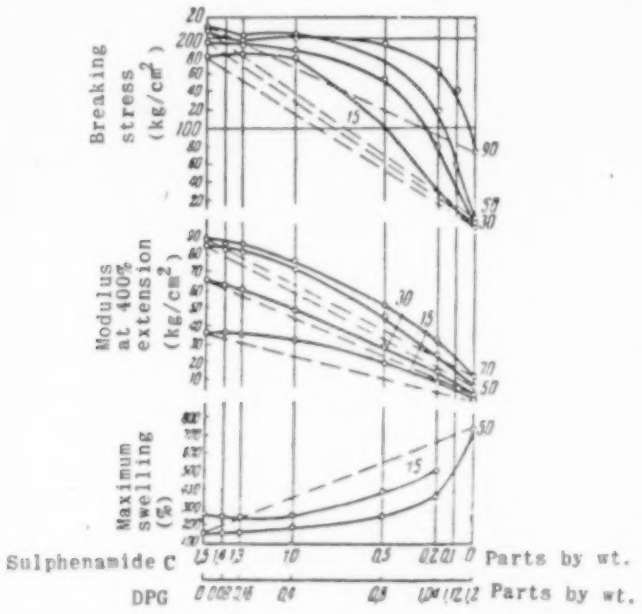


FIG. 6. Activity of the binary system N-cyclohexyl-2-benzothiazylsulphenamide–diphenylguanidine.

Mercaptans and nitrogenous organic bases. These combinations of accelerators are similar in activity to the disulphide-organic base systems. In particular the vulcanization activity of the 2-mercapto-benzothiazol–diphenylguanidine system (Fig. 8) is similar to that of the di-2-benzothiazyl disulphide–diphenylguanidine system (see Fig. 1). A clearly defined mutual activation of the accelerators is found.

Sulphenamides or disulphides and tetramethylthiuram monosulphide. The activity of tetramethylthiuram monosulphide was investigated in conjunction with N,N-diethyl-2-benzothiazolsulphenamide and N-cyclohexyl-2-benzothiazol-

sulphenamide, and also with di-2-benzothiazyldisulphide in the proportion calculated from the optimal concentration of the sulphenamides. These accelerator combinations display approximately additive activity, as is seen from

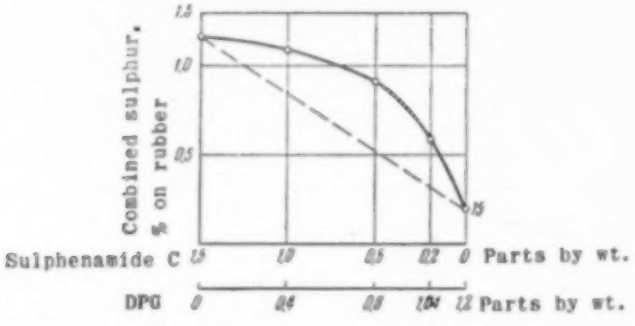


FIG. 7. Variation in combined-sulphur content on vulcanization in the presence of *N*,*N*-diethyl-2-benzothiazolsulphenamide and diphenylguanidine.

Figure 9 which shows the kinetics of vulcanization of the rubber mixtures in the presence of N-cyclohexyl-2-benzothiazol-sulphenamide–tetramethylthiuram monosulphide. The change in the values of tensile strength, modulus and relative

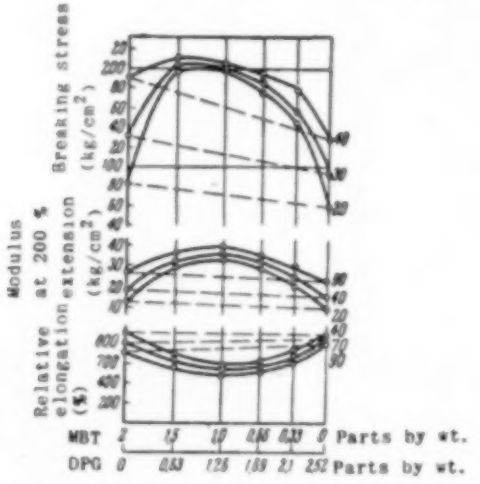


FIG. 8. Activity of the binary system 2-mercaptobenzothiazole–diphenylguanidine.

elongation of the mixtures on vulcanization follows curves close to the dotted lines characterising the additive effect of the accelerators. Binary systems of accelerators in which the components belong to the same class of chemical compound, in particular combinations of N-cyclohexyl-2-benzothiazolsulphenamide with *N*,*N*-diethyl-2-benzothiazolsulphenamide, show a similar activity.

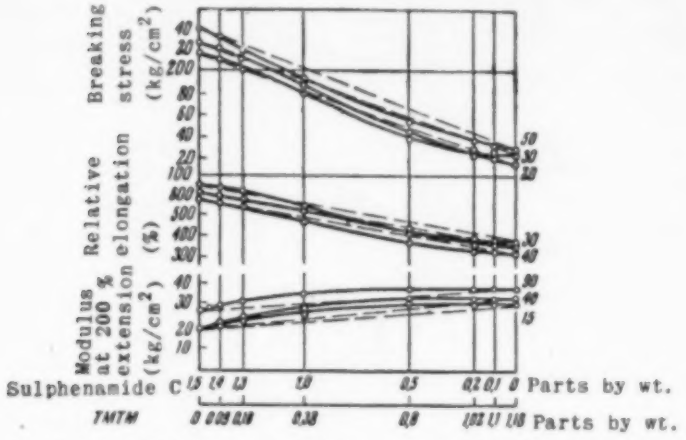


FIG. 9. Activity of the binary system N-cyclohexyl-2-benzothiazolsulphenamide–tetramethylthiuram monosulphide.

THE INTERACTION OF VULCANIZATION ACCELERATORS IN A SOLVENT MEDIUM

The interaction between di-2-benzothiazyl disulphide and diphenylguanidine. 0·71 g of C.P. di-2-benzothiazyl disulphide and 0·45 g of C.P. diphenylguanidine were placed in glass ampoules and 30 ml of xylene was added. The ampoules were sealed and placed in a thermostat at 140°. The ampoules were opened after varying periods of time. The reaction mixtures were treated with cold, 1% sodium hydroxide solution in order to extract the probable reaction product, 2-mercaptobenzothiazole. The latter was precipitated from the alkaline solution by means of dilute hydrochloric acid. Figure 10, Curve I shows the yield of 2-mercaptobenzothiazole in this reaction.

The maximal yield of 2-mercaptobenzothiazol was 3·16 g/litre, corresponding to 30 per cent of theory if it is assumed that the reaction involves equimolar proportions. In view of the difficulty of isolation we did not succeed in finding any other reaction products.

The interaction between di-2-benzothiazyl disulphide and diphenylguanidine in the presence of 0·55 g of sulphur (an equimolar proportion with respect to the disulphide) gave a higher yield of 2-mercaptobenzothiazol. Curve II of Figure 10 shows the kinetics of the reaction in this case.

The interaction between di-2-benzothiazyl disulphide and hexamethylenetetramine. 0·71 g of C.P. di-2-benzothiazyl disulphide and 0·3 g of C.P. hexamethylenetetramine were placed in glass ampoules together with 30 ml of xylene. The sealed ampoules were heated in a thermostat for varying times at 140°, 160° and 170°. In the experiments at 160° and 170° a white-spirit fraction, purified from unsaturated compounds and having a boiling range of 150–180°, was used in place of xylene. The yields of 2-mercapto-benzothiazole from this reaction are shown in Figure 11.

At 140° the yield of the mercaptan from this reaction is much lower than that from the reaction between di-2-benzothiazyl disulphide and diphenylguanidine. An increase in reaction temperature leads to an increased yield of 2-mercaptobenzothiazol.

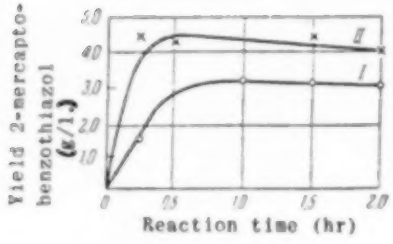


FIG. 10. Yield of 2-mercaptobenzothiazole from the reaction of di-2-benzothiazyldisulphide with diphenylguanidine in xylene at 140° in the presence of sulphur (II) and without sulphur (I).

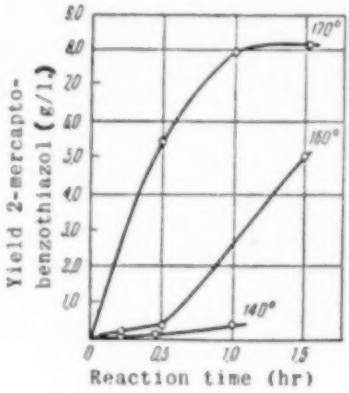


FIG. 11. Yield of 2-mercaptobenzothiazole from the reaction of di-2-benzothiazyldisulphide with hexamethylenetetramine at 140°, 160° and 170°.

The interaction between N-cyclohexyl-2-benzothiazolsulphenamide and di-2-benzothiazyl disulphide and diphenylguanidine. 1·0 g of C.P. N-cyclohexyl-2-benzothiazolsulphenamide and 1·2 g of C. P. di-2-benzothiazyl disulphide in one case and 1·0 g of the sulphenamide with 0·8 g of diphenylguanidine, in the other, were placed in ampoules with 30 ml of solvent (xylene or white spirit). The ampoules were sealed and heated at 150, 160 and 170°. No 2-mercaptobenzothiazole was found.

THE INTERACTION OF VULCANIZATION ACCELERATORS IN THE PRESENCE OF A RUBBER

Experiments on the interaction of accelerators in the presence of a rubber were again carried out in sealed ampoules with the only difference that instead of solvent the ampoules were filled with a 2·5% solution of purified sodium-butadiene rubber (SKB-pishche voi) in xylene. The purification of SKB from alkali was carried out by the method of Dobromyslova [5].

2-Mercaptobenzothiazole separated from the reaction mixture at the end of the reaction. The yields of the mercaptan obtained from the reaction of a number of accelerator systems in the rubber solution are given in the table.

Figure 12 shows results on the separation of 2-mercaptobenzothiazole from the reaction between di-2-benzothiazyl disulphide and N-cyclohexyl-2-benzo-

thiazol-sulphenamide (taken in various proportions), on heating in the rubber solution. In this case the yield of mercaptan is rather high in comparison with what would be expected if the activities of the accelerators were not interdependent (dotted line in Fig. 12).

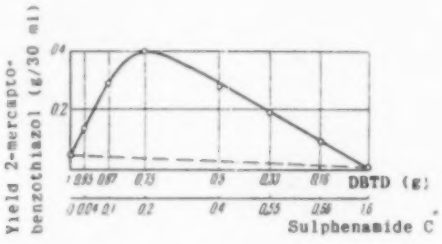


FIG. 12. Yield of 2-mercaptobenzothiazole from the reaction of di-2-benzothiazyldisulphide with N-cyclohexyl-2-benzothiazolsulphenamide on heating in a rubber solution. Time of heating, 90 min; temperature 150°.

DISCUSSION

The experimental results presented above show that binary systems of accelerators can be divided into three classes according to their vulcanization activities: (1) Systems in which the accelerators show marked mutual activation. (2) Systems in which one (the less active) accelerator is activated. As has already been noted above, the vulcanization activity of such systems does not exceed that of the more active accelerator when used alone. (3) Systems in which the activity of the vulcanization accelerators is additive.

Within the limits of each system the vulcanization activity depends on the ratio of the accelerators.

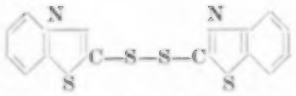
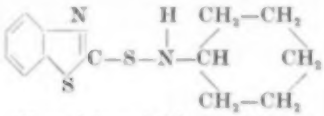
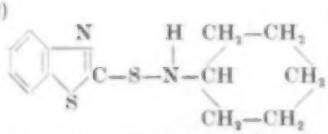
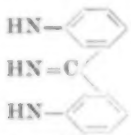
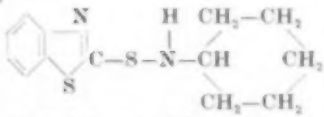
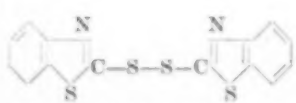
Combinations of disulphides or mercaptans with nitrogenous organic bases and also combinations of disulphides with sulphenamides belong to the class of systems showing marked mutual activation of the accelerations.

Combinations of sulphenamides with nitrogenous organic bases belong to the class of systems in which one of the accelerators is activated.

Additivity of accelerator activity is characteristic of systems consisting of sulphenamides (and some disulphides) and tetramethylthiuram monosulphide, and also of combinations of accelerators belonging to the same class of chemical compounds.

The formation of 2-mercaptobenzothiazole by the interaction of accelerators in a solvent (the reaction between di-2-benzothiazyl disulphide and diphenylguanidine or hexamethylenetetramine) and also in the presence of a rubber (N-cyclohexyl-2-benzothiazolsulphenamide) and di-2-benzothiazyl disulphide or diphenylguanidine) indicates that in the cases in question chemical interaction takes place between the accelerators.

TABLE 1. YIELD OF 2-MERCAPTOBENZOTHIAZOL ON INTERACTION OF ACCELERATORS IN SOLVENTS IN RUBBER SOLUTION (REACTION TIME — 1·5 HR)

Reactants	Characteristic chemical bond of the reactants	Weight of reactants g/30 ml of solution	Yield of 2-mercaptobenzothiazol			
			In xylene at 150°	In white spirit		In 2·5% SKB rubber solution at 150°C
				160°C	170°C	
(1)  Di-2-benzothiazyldisulphide	–S–S–	1·0 + 1·26	—	—	—	0·83
 N-cyclohexyl-2-benzothiazolsulphenemide	–S–N–	0·5 + 0·63	Trace	—	—	0·40
(2)  N-cyclohexyl 1-2-benzothiazolsulphenamide	–S–N–	1·0 + 0·8	—	—	—	0·25
 Diphenylguanidine	–N–H–	0·71 + 0·57	Trace	Nil	Nil	0·17
(3)  N-cyclohexyl 1-2-benzothiazolsulphenamide	–S–N–	1·0	Nil	Nil	Nil	0·025
(4)  Di-2-benzothiozyldisulphide	–S–S–	1·26 0·63	Nil	Nil	—	0·15 0·08

Hence our results are not in accord with the idea, put forward by a number of investigators [1, 2, 3], that activation of accelerators used conjointly is brought by the formation between them of salt-type molecular compounds that have a higher vulcanization activity.

The views outlined below on the mechanism of the joint action of accelerators is a further development of our ideas on the free-radical action of vulcanization accelerators [6, 7, 8].

There are grounds for the assumption that in the joint application of accelerators, free radicals are formed as a result of reactions taking place among them. The formation of free radicals can occur both as a result of thermal decomposition of the accelerators and by chemical reaction between them. The latter obviously takes place with a lower expenditure of energy in comparison with thermal dissociation and hence brings about the greater concentration of free radicals.

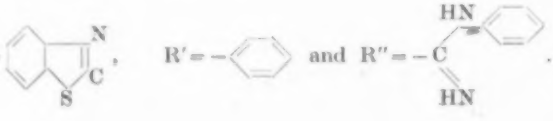
It is known that the chemical behaviour of organic disulphides is, in a number of cases, analogous to that of organic peroxides. Both peroxides and disulphides readily oxidize hydrogen iodide to free iodine—both have a tendency toward thermal and photochemical decomposition to free radicals. As a result of this disulphides, like peroxides, are polymerization initiators [6, 11]. If organic peroxides can form radicals under the action of amines [9, 10], then it may equally be assumed that organic disulphides can also decompose under the action of certain amines to form free radicals. There is no direct reference in the literature to the existence of such reactions, however in the work of Gul'yanova [12] the role of dibutylamine as a catalyst for exchange reactions between organic disulphides and polysulphides, which proceed by a free-radical mechanism, was noted.

We suggest that under the conditions of vulcanization the reaction between disulphides and nitrogenous organic bases (in particular, between di-2-benzothiazyl disulphide and diphenylguanidine) takes place according to the following scheme.

1. $RSSR + R'R''NH \longrightarrow \begin{bmatrix} RSSR \\ R'R''NH \end{bmatrix} \longrightarrow RSH + RS^{\cdot} + R'R''N^{\cdot}H$ — chain initiation
2. $RS^{\cdot} + R'R''NH \longrightarrow RSH + R'R''N^{\cdot}$
3. $R'R''N^{\cdot} + RSSR \longrightarrow RNSR''R' + RS^{\cdot}$
4. $RSSR + RSNR'R'' \longrightarrow \begin{bmatrix} RSSR \\ RSNR'R'' \end{bmatrix} \longrightarrow 3RS^{\cdot} + R''R'N^{\cdot}$

   (2–4: chain propagation)
5. $RS^{\cdot} + R''R'N^{\cdot} \longrightarrow RSNR'R''$
6. $RS^{\cdot} + RS^{\cdot} \longrightarrow RSSR$
7. $R'R''N^{\cdot} + R'R''N^{\cdot} \longrightarrow R'R''NNR''R$

   (5–7: chain termination)

where 

The radicals formed by interaction of the accelerator can initiate other radical processes and in particular the crosslinking of rubber molecules in the vulcanization process.

The isolation of 2-mercaptobenzothiazole as one of the products of reaction between di-2-benzothiazyl disulphide and diphenylguanidine at 140° in xylene supports the suggested scheme to a certain extent. It was not possible to find the two other end products of the reaction (according to the scheme)—benzothiazolylsulphendiphenylguanidine (RSNR′R″) and bis-diphenylguanidine (R′R″ NNR″R′) — because of the difficulty of isolating them from the reaction mixture.

It should be noted that this scheme includes stages (3, 5) involving the formation of compounds of the sulphenamide type, which at the present time are widely used vulcanization accelerators. According to the scheme sulphenamides can themselves give rise to radical decomposition of disulphides (stage 4). This supports the results of the investigation of the reaction between di-2-benzothiazyl disulphide and N-cyclohexyl-2-benzothiazolsulphenamide, i.e. the lack of formation of 2-mercaptobenzothiazole on reacting in a pure solvent, and its abundant formation in the presence of a rubber, which is a hydrogen donor (Figure 12 and table). The formation of considerably more 2-mercaptobenzothiazole than would be found if the activities of the accelerators reacting in the given system were not mutually interdependent, indicates that the main result of the chemical interection of the accelerators is the formation of considerable quantities of free radicals, which abstract hydrogen from the molecular chains of the rubber with formation of polymeric rubber radicals. This also explains the mutual activation in systems of disulphides with both nitrogenous organic bases and sulphenamides.

The activation of accelerators in the mercaptan—organic-base system is also obviously connected with the occurrence of radical reactions between the accelerators.

This is also true of systems of sulphenamides with nitrogenous organic bases. It is known that amines are capable of mutual displacement from their derivatives [13]. On the basis of this we consider that sulphenamides and amines can react with one another with the intermediate formation of free radicals according to the equation:

$$RS{-}NR_1R_2 + HNR'R'' \longrightarrow \left[\frac{RSNR_1R_2}{HNR'R''}\right] \longrightarrow [RS^{\cdot} + {}^{\cdot}NR'R''] + HNR_1R_2$$

The absence of mutual activation of the accelerators in systems with additive activities indicates that in such cases the presence of one accelerator does not affect the production of radicals of the other.

CONCLUSIONS

(1) It has been established that in the joint action of vulcanization accelerators, depending on their chemical structure, mutual activation of the accelerators, or one of them is activated, or their effect is additive.

(2) Of the combinations of vulcanization accelerators investigated disulphides or mercaptans with nitrogenous organic bases, and also disulphides with sulphenamides are systems displaying mutual activation. Combinations of sulphenamides with nitrogenous organic bases are systems characterized by activation of one of the accelerators. Examples of accelerator systems with additive activities are combinations of sulphenamides or disulphides with tetramethylthiuram monosulphide.

(3) It has been found that in the case of systems showing mutual activation, such as di-2-benzothiazyldisulphide and diphenylguanidine, or di-2-benzothiazyldisulphide and N-cyclohexyl-2-benzothiazolsulphenamide, interaction of the accelerators leads to formation of 2-mercaptobenzothiazole. In these systems, under vulcanization conditions, a larger yield of 2-mercaptobenzothiazol is found than would be formed by separate action of the accelerators. This indicates that the main result of the chemical interaction of the accelerators is the formation of free radicals which are capable of abstracting hydrogen from the rubber molecules with formation of polymeric, rubber radicals.

(4) An illustrative scheme is put forward for the radical mechanism of joint action of vulcanization accelerators for the case of systems with mutual activation of the accelerators.

Translated by E. O. PHILLIPS

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THE HETEROGENEOUS POLYMERIZATION OF SODIUM ACRYLATE IN THE PRESENCE OF OTHER SALTS*

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(*Received* 14 *July* 1959)

A NUMBER of papers have appeared in recent years, devoted to the study of polymerization of monomers in the solid state [1–5]. In order to bring about such processes high-energy radiation is normally used. In the present work we have been able to show that for initiation of polymerization of crystalline monomers one can also make use heterogeneous chemical reactions.

In a study of the systems sodium acrylate–LiCl and sodium acrylate–$MgCl_2$ we have found that if a 50% solution of ethanol in water is added to crystalline mixtures of sodium acrylate and lithium or magnesium chlorides, sufficient only to moisten the crystals, rapid polymerization of the acrylate takes place. Polymerization begins immediately on moistening the crystals. The polymerization proceeds very effectively on moderate heating. As a result of the reaction the mixture of crystals in the system is converted to a solid, continuous mass which swells only very slightly in an excess of 50% ethanol.

In order to bring about the reaction the process of mixing the solid salts with the solvent must be carried out in a thoroughly evacuated system and the solvent must be degassed previously. If the solvent is added to the mixed salts in air and the dissolved gases are removed after moistening the mixture, then polymerization does not occur even on heating for 50 hours at 100° in a sealed ampoule. This result, which was reproduced many times, indicates that the polymerization process is brought about by a reaction that occurs immediately on moistening the mixture of solid, crystalline salts, and that this reaction is ineffective if it takes place in air. This reaction is in all probability, the exchange reaction between sodium acrylate and lithium or magnesium chloride, as a result of which a new solid phase, sodium chloride, is formed in the system, and this is less soluble in aqueous alcohol than the original salts. In fact it is not difficult to confirm that on mixing concentrated solutions of sodium acrylate and lithium or magnesium chloride in 50% alcohol sodium chloride is precipitated.

* Vysokomol. soedin. 1: No. 2, 301–307, 1959.

The supposition that the exchange reaction leading to the formation of a new solid phase in the system is the source of initiation of polymerization is confirmed by the fact that in a mixture of lithium acrylate–LiCl–50% alcohol, prepared under similar conditions but where of course a new solid phase does not form, practically no polymerization occurs even on prolonged heating in sealed ampoules.

The following experimental method was used. Weighed quantities of the salts were placed in the ampoule 1 (Fig. 1), which has one wide and two narrow side tubes, inside a dry chamber. (The dry chamber in necessary because of the hygroscopic nature of LiCl.) The wide tube was then sealed and ampoule 2 was sealed on to one of the side arms of ampoule 1. The other tube was sealed to a vacuum line. The required amount of aqueous alcohol was then placed in ampoule 2 through the open tube, which was then sealed. The charge in ampoule 2 was next frozen in liquid nitrogen and the pressure in the system was taken down to 10^{-6} mm Hg. The system was then isolated from the vacuum line by means

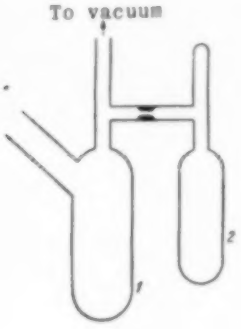

FIG. 1.

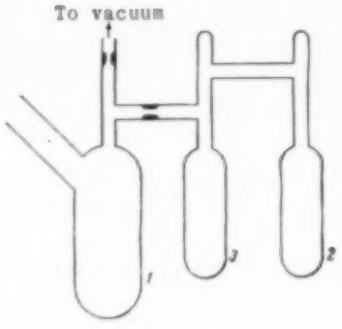

FIG. 2.

of a cock and the solvent in ampoule 2 was melted. This resulted in liberation of the dissolved gases. This operation was repeated until, after successive melting and freezing, the pressure in the system ceased to rise (6–8 times). Next the system of joined ampoules under vacuum was removed from the vacuum line, the solvent melted, and ampoule 1 containing the crystalline salts was cooled in liquid nitrogen. As a result of this the solvent in ampoule 2 passed over into ampoule 1 via the vapour phase. At the end of the distillation ampoule 1, containing the mixture of salts and frozen solvent, was disconnected from ampoule 2 and placed in a thermostat heated to the required temperature.

When, in addition to 50% alcohol, it was required to add a third solid phase, soluble in the solvent mixture, ampoule 3 was sealed in between ampoules 1 and 2 (Fig. 2), and the substance to be added was placed in this. In this case the melted solvent was distilled from ampoule 2 into ampoule 3, from which the solution of the third solid phase was poured into ampoule 1.

After polymerization ampoule 1 was opened and the polymer formed was washed free from low-molecular salts with 50% ethanol until the washings gave a negative reaction for chloride ions. When it was required to determine the quantity of polymer formed, in order to calculate the degree of conversion, after washing free from low-molecular salts the polymer, in the form of a swollen but insoluble gel, was treated several times with aqueous hydrochloric acid and then washed again with 50% ethanol to a negative reaction for chloride ions. The polymeric mixed salt was thereby converted to the polyacid. The complet-

eness of conversion was assessed by the colour of the flame on burning the polymer and by an ash determination. The polyacid was dried and weighed.

In order to determine the effect of the state of aggregation of the salts on the polymerization process the following experiments were set up.

(1) Instead of mixing crystalline sodium acrylate with crystalline lithium chloride and subsequent addition of 50% alcohol *in vacuo*, saturated solutions of these salts in 50% alcohol were mixed. Mixing of the solutions was also carried out in vacuo. Before mixing, each solution was thoroughly degassed separately. In this case crystalline sodium chloride precipitated as soon as the salt solutions were mixed, however practically no polymer was formed either at the moment of precipitation of NaCl or on subsequent heating in sealed ampoules for 24 hours at 100°.

(2) A saturated solution of sodium acrylate was added to crystalline LiCl *in vacuo*. In this case also practically no polymerization occurred either in mixing the components or on subsequent heating in sealed ampoules. On heating only an extremely small quantity of low-molecular polymer was formed, which was soluble in 50% ethanol.

(3) A solution of LiCl in 50% ethanol was added to crystalline sodium acrylate. In this case polymerization proceeded almost as effectively as in the case of addition of solvent to the mixture of crystalline salts.

The experiments described indicate that in order to bring about polymerization in the system sodium acrylate–LiCl it is necessary that the monomer should be in the crystalline state and that in the exchange reaction between the salts, taking place in the heterogeneous system, a new crystalline phase, sodium chloride, should be formed.

We studied the dependence of the degree of conversion of monomer on polymerization time for the system sodium acrylate–LiCl at 80°.

TABLE 1. THE DEPENDENCE OF THE DEGREE OF CONVERSION OF SODIUM ACRYLATE ON POLYMERIZATION TIME IN THE PRESENCE OF LITHIUM CHLORIDE

Temperature 80 ± 0·1°C Wt. of sodium acrylate – 2·02 g Quantity of 50% C_2H_5OH – 3·0 ml

Time (min)	Weight of LiCl(g)	Conversion	Time (min)	Weight of LiCl(g)	Conversion
5	3·00	4	60	3·20	52
10	3·25	24	120	3·24	57
20	3·15	37	180	3·21	58
20	3·21	35	240	3·37	55
30	3·19	49	300	3·3	52
			420	2·87	60

Polymerization was carried out by addition of 50% ethanol to a mixture of the crystalline salts. The commencement of polymerization was taken as the

moment of immersion of the ampoule, containing the mixture of salts and frozen solvent, in the thermostat. At chosen intervals an ampoule, with the reaction mixture, was removed from the thermostat, opened, and the polymeric salt, according to the method described above, was washed free from low-molecular salts and converted to the polyacid which was then dried and weighed.

The results are shown in Table 1 and Figure 3 which has the polymerization time as abscissa and the degree of polymerization as ordinate.

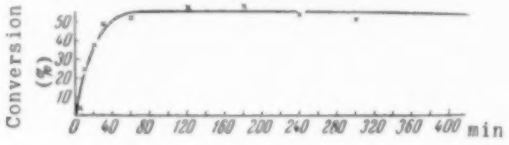

FIG. 3. The dependence of the percentage conversion of monomer on polymerization time.

It is seen that in this system polymerization begins immediately on melting the solvent, without an induction period, and practically ceases after 30 minutes. The rising section of the curve in Figure 3 becomes a straight line in the coordinates logarithm of time–percent conversion.

At low temperatures the rate of polymerization is evidently controlled by the rate of distribution of the solvent in the system and its diffusion through the polymer phase already formed.

We were able to confirm this visually by means of the following experiments.

In place of ampoule 1 (Fig. 1) an ampoule 1a was used, the bottom of which was drawn out to a long, thin-walled capillary (Fig. 4) which was filled with the mixture of sodium acrylate and LiCl. In other respects the experiment was carried out by the method described above. During the distillation of the solvent from ampoule 2 into ampoule 1a the latter was deeply immersed in liquid nitrogen in a Dewar vessel. Consequently the solvent was held in the upper part of ampoule 1a, forming a solid layer on its walls. At the end of the distillation ampoule 1a was disconnected and placed before the objective of a horizontal microscope so that the penetration of the melting solvent into the mixture of salts in the capillary could be observed. The experiments were carried out at room temperature (20°).

In fact, it was seen in the microscope that as the solvent diffused down the salts in the capillary formation of a readily swelling, polymeric mass took place rapidly in the moistened part of the salt column. At almost any moment of time the moving boundary between the moistened and unmoistened part of the salt mixture in the capillary simultaneously formed the boundary between the polymeric and monomeric phases. During the course of the experiment penetration of the liquid down the salts in the capillary rapidly lessened because of the difficulty of diffusion through the polymeric mass which forms in the upper part of the capillary.

Subsequently it was found that polymerization can take place at −30°, −40° and even at −50°, in the system sodium acrylate–LiCl–aqueous ethanol. For polymerization at these temperatures 50%, 70% and 80% ethanol was used, respectively. The quantity of polymer formed in these circumstances was

less than that formed by high-temperature polymerization. This is connected with the extremely low rate of diffusion of the solvent at these temperatures. On coming into contact with the solvent the crystalline mixture becomes enveloped in a layer of polymer and further diffusion of solvent into the depth of the system is almost completely prevented.

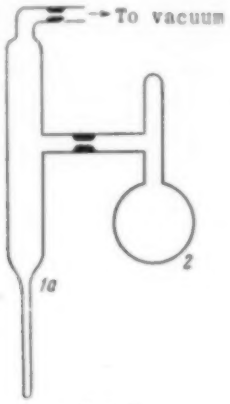

FIG. 4.

The fact that polymerization occurs at such low temperatures is very interesting. It indicates that the active centres formed in the system as a result of the exchange reaction between the salts are highly reactive and do not require additional thermal activation. At the same time steric hindrance, which arises in the process of combination of the units of a polymer chain, is very slight as a result of the ordered and relatively fixed disposition of these units in the crystal lattice. It is interesting that the molecular weight of the polyacrylates formed by polymerization at low temperatures is lower than that of the polymers formed at high temperatures.

The addition to the system of a typical radical inhibitor, hydroquinone, together with the solvent, did not inhibit polymerization when added in the proportion of 1% on the weight of monomer.

The hydroquinone was introduced in the following way. The weighed amount of hydroquinone was placed in the intermediate ampoule 3 (Fig. 2) into which the degassed solvent was distilled from ampoule 2. The hydroquinone was dissolved in the aqueous alcohol and the solution, prepared *in vacuo*, was poured into ampoule 1, containing the crystalline salts.

It was of interest to examine whether there is any relationship between the quantity of lithium chloride in the system and the quantity of polymer formed. For this purpose we determined the yield of polymer from reaction mixtures containing constant amounts of sodium acrylate and 50% alcohol and varying quantities of LiCl, after heating for 2 hours. Polymerization was carried out in a thermostat at $80 \pm 0{\cdot}1°$. Examination of Figure 2 shows that polymerization would already have ceased in the system after this time at the given temperature.

The results of these measurements are shown in Table 2 and Figures 5 and 6. Figure 5, which has the quantity of added lithium chloride in grammes as abscissa and the limiting degree of conversion as ordinate, shows that with a low LiCl content in the mixture, as this content increases the degree of conversion increases

TABLE 2. THE DEPENDENCE OF THE LIMITING DEGREE OF CONVERSION ON THE LiCl CONTENT

Polymerization time, 2 hr. Temperature, 80±0·1°C.
Weight of acrylate, 2·02 g. Quantity of 50% C_2H_5OH, 3·0 ml.

Weight of LiCl (g)	Conversion (%)
0·13	16
0·24	29
0·31	50
0·58	58
1·18	59
3·24	58
4·58	33
5·24	14
6·73	9
9·69	5

and then reaches a limiting value. On further increasing the proportion of lithium chloride the degree of conversion decreases. It should be noted that over the interval of concentration of LiCl in which the percentage of monomer converted

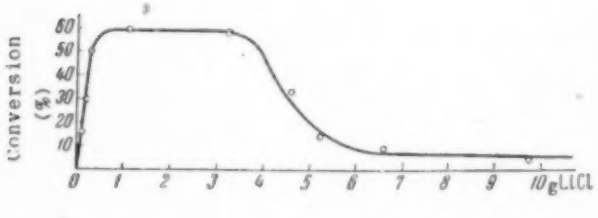

FIG. 5. The dependence of the limiting degree of conversion on the LiCl content of the system.

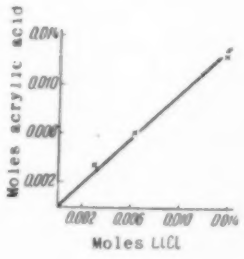

FIG. 6. The dependence of the number of moles of monomer polymerized, on the number of moles of LiCl present in the system.

increases, the number of moles of monomer polymerized is equal to the number of moles of lithium chloride added (Fig. 6). This again indicates that the exchange reaction between the salts, taking place in a heterogeneous system, is closely connected with the initiation process.

Similar experiments were set up to establish the relationship between the quantity of solvent in the system and the limiting degree of conversion. In this case the quantities of sodium acrylate and lithium chloride were kept constant each time and the amount of 50% ethanol was varied. Polymerization was carried out for 2 hours at $80 \pm 0{\cdot}1°$. The results are shown in Table 3 and Figure 7, which has the number of millilitres of solvent added as abscissa and the limiting degree of conversion as ordinate. It is seen that for the ratio of the salts taken there is a definite optimal quantity of solvent at which the percentage conversion reaches a maximum.

TABLE 3. THE DEPENDENCE OF THE LIMITING DEGREE OF CONVERSION ON THE QUANTITY OF 50% C_2H_5OH ADDED

Weight of acrylate, 2·02 g

Weight of LiCl (g)	50% C_2H_5OH (ml)	Conversion (%)
3·46	0·5	5
3·63	1	10
3·29	2	27
3·24	3	60
3·46	5	21
3·35	6	10
3·24	10	5

It was stated in the beginning of the paper that after polymerization the reaction mixture is a solid, continuous mass that scarcely swells at all on first washing with 50% ethanol. Subsequently, as the low-molecular salts are removed the swelling of the polymer increases considerably. It may naturally be assumed that the solidification, or "enclosing" of the reaction mass is brought about by the formation of a crystalline structure arising as a result of the occurrence of non-equilibrium contacts between the NaCl crystals, "generated" under conditions of high relative supersaturation, and the crystals of the monomer salt. It may be considered that initiation of polymerization is these systems is in fact connected with the occurrence of such contacts. (Note that in polymeric media such non-equilibrium contacts must be of considerably longer duration.) It is possible that in the case in question the source of initiation is the excess free surface energy of the NaCl crystals formed which causes non-equilibrium contacts between the NaCl crystals and the crystals of the monomer salt. Defects in the crystal structure arising at the points of contact, for example "superfluous" ions "stack" in the monomer lattice.

If it is accepted that the formation of such contacts is a component part of the initiation process the character of the curves of Figures 5 and 6 can be explained. Thus for example, the fall in the degree of conversion with increasing quan-

tity of LiCl in the system, at constant concentrations of monomer and solvent (Fig. 5), can be explained in the following way. An excessive increase in the quantity of the solid, hydratable component (LiCl) in the system results in there being an insufficient quantity of solvent to bring about successfully the exchange reaction and the formation of a new phase. This idea can also explain the maximum in the curve for the dependence of the limiting degree of conversion on the

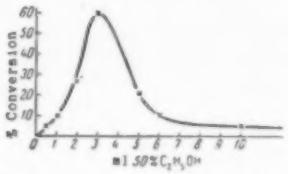

FIG. 7. The dependence of the limiting degree of conversion on the quantity of solvent.

quantity of solvent in the system with constant sodium acrylate and lithium chloride contents. Small quantities of solvent are insufficient for the reason already stated and too much hinders the formation of the necessary crystallization contacts.

In order to verify the hypothesis concerning the effect of crystallization contacts on the polymerization process we used a 1% solution of a surface-active substance (sodium oleate) in aqueous alcohol, as solvent. It was found that in this case the limiting degree of conversion of monomer was decreased by a factor of about 3. A similar decrease was observed when the sodium acrylate crystals were treated before polymerization with a solution of acetylcellulose in acetone, and dried. The introduction of a surface active agent which is adsorbed on to the crystals in the first case, and coating the monomer crystals with a thin film of acetylcellulose in the second hinders with the formation of crystallization contacts and consequently hinders the initiation of polymerization.

As already mentioned, polymerization does not occur if the addition of solvent is carried out in air and the dissolved gases are removed only after this stage. This fact can be connected with the following idea. In a system containing dissolved gases the centres of "birth" of the new crystalline phase must also serve as centres of gas formation. Hence the growing crystals in such a system become covered with a gaseous envelope which can prevent initiation.

CONCLUSIONS

It has been shown in this work that in the systems sodium acrylate—LiCl—50% C_2H_5OH and sodium acrylate–$MgCl_2$–aqueous C_2H_5OH the heterogeneous exchange reaction between the salts can be utilized for initiation of the polyme-

rization of crystalline sodium acrylate. The formation of a new solid, crystalline phase and its contacting with the crystals of the monomer salt plays an essential role in the initiation process.

A detailed study of similar reactions and of the properties of the polymers formed is at present being carried out.

Translated by E. O. PHILLIPS

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THE ROLE OF FREE RADICALS IN THE LOW-TEMPERATURE CROSSLINKING (VULCANIZATION) OF RUBBER *

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(*Received* 27 *January* 1959)

VOL. 1 1960

IN SPITE of a large amount of research, the mechanism of the vulcanization process has not yet been completely elucidated. In particular, opinions are divided on the nature of the reactions taking place during vulcanization. One group of investigators considers that the vulcanization process is determined mainly by ionic reactions whereas the other group assumes that they are radical reactions. We have therefore carried out some work with the object of obtaining data on the nature of the reactions involved in the sulphur vulcanization of rubber.

Mild vulcanization conditions were chosen in order to facilitate the study of the mechanism of the reactions taking place on vulcanization. The vulcanization systems used were: di-2-benzothiazyl disulphide (DBTD)–hydrogen sulphide, benzyl peroxide (BP)–hydrogen sulphide, and sulphur dioxide–hydrogen sulphide, which are sources of sulphur *in statu nascendi* at room temperature.

We have established [1] that dibenzothiazyl disulphide reacts with hydrogen sulphide in benzene or toluene at 20°C. according to the equation

$$RSSR + H_2S \longrightarrow 2RSH + S \qquad (1)$$

with a quantitative yield of mercaptobenzothiazole and elementary sulphur (Fig. 1).

No other reaction products were found. Under the same conditions benzoic acid and elementary sulphur were liberated in the reaction between benzoyl peroxide and hydrogen sulphide,

$$(RO_2)_2 + H_2S \longrightarrow 2ROOH + S \qquad (2)$$

but the reaction rate here was considerably lower than that in the first case (Fig. 2) though the –S–S– bond energy is substantially higher than of the –O–O–

* Vysokomol. soedin. 1: No. 2, 315–323, 1959.

bond. On reacting sulphur dioxide with hydrogen sulphide under similar conditions elementary sulphur is liberated according to the well known equation

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S \qquad (3)$$

Because many investigators consider that sulphur *in statu nascendi* is capable of vulcanizing rubber we expected these systems to have a vulcanizing (cross-linking) action on rubber.

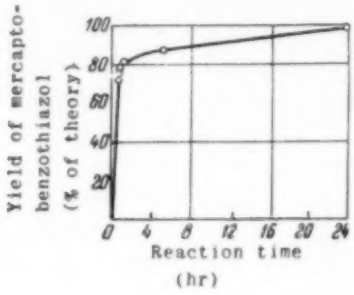

FIG. 1. The kinetics of formation of mercaptobenzothiazole in the reaction of dibenzothiazyl disulphide with hydrogen sulphide in toluene at 20°.

We assessed the vulcanizing activity of these systems according to their ability to bring about gel formation of 5% toluene solutions of the sol fraction of purified sodium-butadiene rubber. For this purpose the chosen quantity of of C.P. dibenzothiazyl disulphide or benzoyl peroxide was added to freshly prepared rubber solutions, after which the solutions were saturated with hydrogen

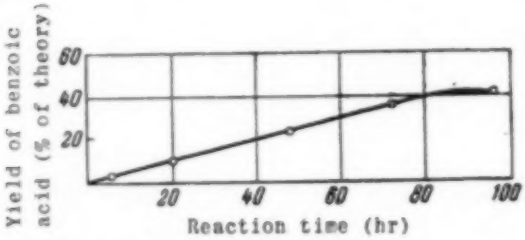

FIG. 2. The kinetics of formation of benzoic acid in the reaction between benzoyl peroxide and hydrogen sulphide in benzene at 20°.

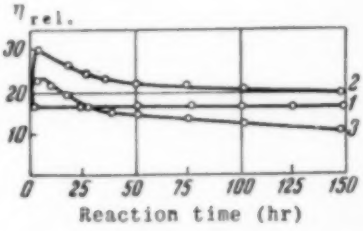

FIG. 3. The variation in relative viscosity of rubber solutions under the action of the system dibenzothiazyl disulphide–hydrogen sulphide (1 — original rubber solution; 2 — 2% DBTD H_2S; 3 — 4% DBTD H_2S).

sulphide and maintained at room temperature. In the case of the sulphur dioxide–hydrogen sulphide system the rubber solutions were previously heated for 30 min at 85–90° and saturated successively with sulphur dioxide and hydrogen sulphide after cooling.

However, in spite of the liberation of sulphur *in statu nascendi* in all these cases, no vulcanization occurred.

For the disulphide–hydrogen sulphide system the variation in relative viscosity of the rubber solutions was measured (Fig. 3), the infrared spectra were plotted and the combined sulphur was determined in both the rubber precipitated from solution by methanol and the residual, unprecipitated portion of the rubber obtained by evaporation of the mother liquor.*

As is seen from the results of analysis of the rubber, as a result of the consecutive action of the disulphide and hydrogen sulphide combination of sulphur with the rubber is not homogeneous, the precipitated fraction (90% by weight) contains practically no combined sulphur (0·04–0·10%) whereas the fraction that is not precipitated by methanol contains 1·2–1·6% combined sulphur. The infrared spectrum of the precipitated portion is similar to that of the original rubber but the 1–4 double-bond content of the unprecipitated portion is reduced by 3% and the 1–2 double-bond content remains unchanged†. Hence from the results obtained it follows that sulphur *in statu nascendi* does not cause vulcanization of rubber solutions. However, data are presented below which indicate that these systems can give rise to vulcanization of rubber at room temperature under certain conditions.

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1. THE SYSTEM DIBENZOTHIAZYL DISULPHIDE–HYDROGEN SULPHIDE

In this case vulcanization takes place if the rubber solution containing the disulphide is irradiated by diffused daylight or ultraviolet light before saturation with hydrogen sulphide. Various vulcanization rates are then obtained, depending on the duration of irradiation (Figs. 4, 5 and 6). From the data presented in the diagrams it is seen that there are definite limits to the irradiation times within which gelation occurs. Below a certain irradiation time, as well as after prolonged irradiation, gelation does not occur.

The existence of a gelation region is evidently connected with the existence of rubber radicals in the solution, resulting from the action on the rubber of short-lived sulphenyl radicals formed by photochemical dissociation of the disulphide. There is a relationship between the variation in relative viscosity of the rubber solutions containing the disulphide, on storing in the light, and their tendency toward gelation under the action of hydrogen sulphide (Figs. 7 and 4). The period of greatest viscosity change corresponds to the gelation region. The presence of mercaptobenzothiazole in the irradiated rubber solutions containing DBTD was shown by a qualitative reaction (formation of lead mercaptide).

* Combined sulphur was determined after boiling the solutions with 10% sodium sulphide solution (to remove free sulphur) and treatment with 1% NaOH solution (to remove mercaptobenzothiazole).

† In our earlier publication [1] it was stated erroneously that the loss of double bonds was much greater.

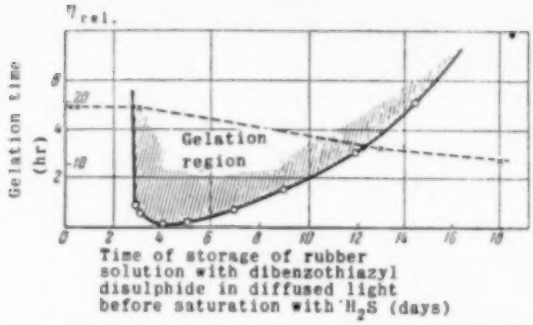
$\eta_{rel.}$
Gelation time (hr)
Gelation region
Time of storage of rubber solution with dibenzothiazyl disulphide in diffused light before saturation with H_2S (days)

FIG. 4. The dependence of the gel time of rubber solutions under the action of hydrogen sulphide on the preliminary storage time with dibenzothiazyl disulphide (4%) in diffused light.

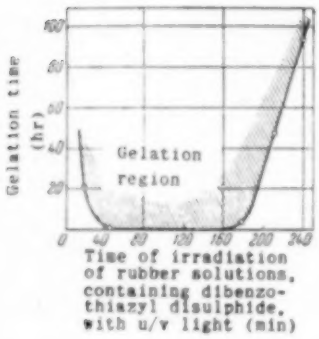
Gelation time (hr)
Gelation region
Time of irradiation of rubber solutions, containing dibenzothiazyl disulphide, with u/v light (min)

FIG. 5. The dependence of the gel time of rubber solutions under the action of hydrogen sulphide on the duration of preliminary ultraviolet-light irradiation in the presence of dibenzothiazyl disulphide (4%).

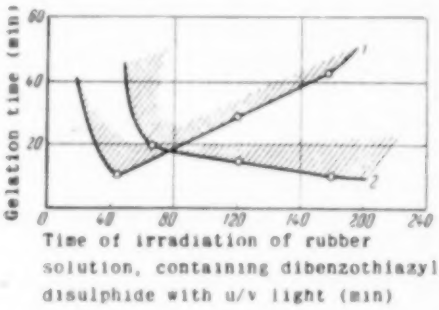

FIG. 6. The dependence of the gel time of rubber solutions under the action of hydrogen sulphide on the duration of preliminary ultraviolet-light irradiation in the presence of dibenzothiazyl disulphide (4%) (1—in air; 2—in nitrogen).

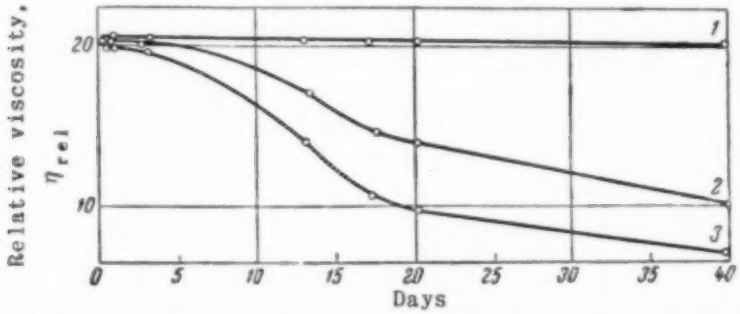

FIG. 7. The variation in relative viscosity of rubber solutions on storage with dibenzothiazyl disulphide in diffused light (1—original rubber solution; 2—with 2% DBTD; 3—with 4% DBTD at 20°).

The composition of the gas phase above the solution affects the rate and extent of gelation. In a medium of nitrogen gel formation starts later but continues longer than in air (Fig. 6).

Vulcanization is inhibited by a number of substances, for example, hydroquinone, phenyl-β-naphthylamine, triethanolamine and diphenylguanidine.

2. THE SYSTEM BENZOYL PEROXIDE–HYDROGEN SULPHIDE

This system vulcanizes the rubber in the presence of an amine (phenyl–β–naphthylamine) but when there is a large excess of phenyl–β–naphthylamin- (at a 20:1 molar ratio of amine to benzoyl peroxide) the system has no crosslinke ing action. These results are not in agreement with those of Dolgoplosk and co-workers [2] who observed gelation of rubber solutions under the action of benzoyl peroxide and hydrogen sulphide and explained it by the occurrence of radical reactions between the peroxide and hydrogen sulphide

$$ROOR + H_2S \longrightarrow ROH + HS^{\cdot} + RO^{\cdot} \qquad (4)$$

In fact, as the above data show, gelation in their experiments evidently occurred as a result of the presence of traces of pnehyl–β–naphthylamine in the rubber and not as a result of reaction (4). Possibly the reaction between benzoyl peroxide and hydrogen sulphide is of the oxidation-reduction, ionic type described by Razuvayev [3], and becomes a radical reaction only in the presence of an amine.

There are reports in the literature on the radical character of the reaction between benzoyl peroxide and certain amines (the work of Bagdasar'yan [4], Chaltykyan [5], Horner [6], Imoto [7] etc).

In order to obtain further confirmation of the radical character of the reaction between a peroxide and an amine we made a special investigation of the reaction between benzoyl peroxide and phenyl–β–napthylamine.

It was found from these experiments that benzoyl peroxide reacts vigorously with phenyl–β–naphthylamine in ether solution at room temperature, with the formation of benzoic acid and O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine. The yield of benzoic acid depends on the ratio of the reactants. At an equimolar ratio the quantity of benzoic acid corresponds to the stoichiometry of a bimolecular reaction. At a 2 : 1 ratio the quantity of benzoic acid formed is greater than that corresponding to the equation of a bimolecular reaction. The reaction product O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine, in the same way as the original amine, brings about decomposition of benzoyl peroxide (with formation of benzoic acid).

On the basis of these results the following scheme for the reaction between a peroxide and an amine can be put forward:

1. $ROOR + R'R''NH \rightarrow [ROOR \cdot R'R''NH] \rightarrow ROH + RO^{\cdot} + R'R''N^{\cdot}$ chain initiation
2. $RO^{\cdot} + R'R''NH \rightarrow ROH + R'R''N^{\cdot}$
3. $R'R''N^{\cdot} + ROOR \rightarrow R'R''NOR + RO^{\cdot}$ } chain propagation
4. $ROOR + RONR'R'' \rightarrow [ROOR \cdot RONR'R''] \rightarrow 3RO^{\cdot} + {}^{\cdot}NR'R''$
5. $RO^{\cdot} + R'R''N^{\cdot} \rightarrow RONR'R''$
6. $RO^{\cdot} + RO^{\cdot} \rightarrow ROOR$ } chain termination
7. $R'R''N^{\cdot} + R'R''N^{\cdot} \rightarrow R'R''NNR'R''$

where $R = C_6H_5CO$, $R' = C_6H_5$ and $R'' = C_{10}H_7$

We then found that O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine initiates the vulcanizing action of the system benzoyl paroxide–hydrogen sulphide more vigorously than the original amine. The addition of small quantities of O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine caused instantaneous gelation of the rubber solutions. In a number of cases vulcanization was so extensive that the gel was obtained in a granular form. Such vigorous gel formation was not observed in the case of phenyl–β–naphthylamine.

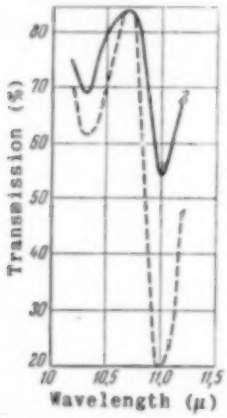

FIG. 8. Infrared spectrum of the gel obtained on vulcanization with the system dibenzothiazyl disulphide–h_F–hydrogen sulphide in the double -bond absorption– band region (1 – spectrum of original rubber; 2 – spectrum of gel).

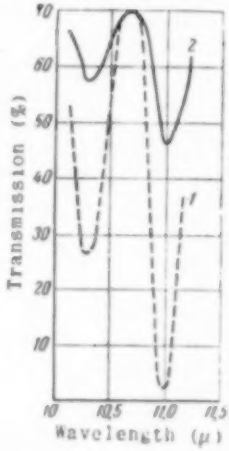

FIG. 9. Infrared spectrum of the gel obtained on vulcanization with the system benzoyl peroxide–hydrogen sulphide, in the presence of phenyl–β–naphthylamine in the double-bond absorption-band region (1 – spectrum of original rubber; 2 – spectrum of gel).

THE SYSTEM SULPHUR DIOXIDE–HYDROGEN SULPHIDE

This system shows vulcanizing activity with freshly prepared, unheated rubber solutions. Gel formation occurs in 1·5–2 hr after saturating the solutions with the gases.

If the solution is heated at 90° for 30 min before saturation with the gases gel formation does not occur. Hydroquinone, diphenylguanidine and phenyl–β–naphthylamine inhibit the vulcanizing action of this system. The inhibiting action of these additives, and also of preliminary heating, is evidently connected with the decomposition of peroxide groups in the rubber itself, that are necessary for the initiation of vulcanization.

The combined-sulphur content of the gels obtained with DBTD and hydrogen sulphide, and with BP and hydrogen sulphide, was 0·6–0·7%. The infrared spectra of the gels showed that 27% of the 1–4, and 60% of the 1–2 double-bonds had disappeared in the first case. Vulcanization with the system benzoyl peroxide–amine–hydrogen sulphide led to the disappearance of 60% of the 1–4, and 75% of the 1–2 double-bonds (Figs. 8 and 9).

DISCUSSION

The results obtained— the formation of mercaptobenzothiazole on storing the rubber with dibenzothiazyl disulphide in diffused light, the inhibiting action of amines and hydroquinone on the systems dibenzothiazyl disulphide–hydrogen sulphide and sulphur dioxide–hydrogen sulphide, the nonstoichiometric yield of benzoic acid from the action of benzoyl peroxide on the rubber in the presence of an amine, the disappearance of a large proportion of the rubber double bonds on gel formation, the inappropriate quantity of combined sulphur, the function of preliminary heating on vulcanizing with the Peachey system, and certain other kinetic features observed, enable the conclusion to be drawn that all the cases of low temperature crosslinking (vulcanization) investigated by us take place by a radical mechanism which can be depicted by the following schemes

1. Vulcanization (crosslinking) of rubber with the system dibenzothiazyl disulphide–hydrogen sulphide

1. $RSSR \rightarrow 2RS^{\cdot}$	Chain initiation
2. $RS^{\cdot} + Ka \rightarrow Ka^{\cdot} + RSH$	Chain propagation (stages 5, 6, 7, 8 and 9 are crosslinking reactions)
3. $Ka^{\cdot} + H_2S \rightarrow Ka + HS^{\cdot}$	
4. $Ka + HS^{\cdot} \rightarrow KaSH^{\cdot}$	
5. $Ka^{\cdot}SH^{\cdot} + Ka \rightarrow KaSHKa^{\cdot}$	
6. $KaSHKa^{\cdot} + Ka \rightarrow KaSHKa - Ka^{\cdot}$ etc.	
7. $Ka + Ka^{\cdot} \rightarrow Ka - Ka^{\cdot}$	
8. $Ka + Ka - Ka^{\cdot} \rightarrow Ka - Ka - Ka^{\cdot}$ etc.	
9. $Ka^{\cdot} + Ka^{\cdot} \rightarrow Ka - Ka$	Chain termination

where Ka is a rubber molecule; ROOR, benzoyl peroxide; RSSR, dibenzothiazyl disulphide; Ka˙, a polymeric, rubber hydrocarbon radical formed by abstraction of a hydrogen atom from an α–methylene group or a tertiary carbon atom; KaSH˙, a polymeric radical formed by the addition of HS˙ to a double bond of a rubber molecule and Ka–Ka˙, a polymeric radical formed by the addition of Ka˙ to the double bond of a rubber molecule.

2. VULCANIZATION (CROSLINKING) OF RUBBER WITH THE SYSTEM PEROXIDE + AMINE + HYDROGEN SULPHIDE

1. $ROOR \xrightarrow{NH'R'';\ RONR'R''} RO^{\cdot}$ and other radicals according to the scheme on page 120 above — Chain initiation
2. $RO^{\cdot} + H_2S \rightarrow ROH + HS^{\cdot}$
3. $RO^{\cdot} + Ka \rightarrow ROH + Ka^{\cdot}$
4. $Ka^{\cdot} + H_2S \rightarrow Ka + HS^{\cdot}$
5. $Ka + HS^{\cdot} \rightarrow KaSH^{\cdot}$
6. $KaSH^{\cdot} + Ka \rightarrow KaSHKa^{\cdot}$
7. $KaSHKa^{\cdot} + Ka \rightarrow KaSHKa - Ka^{\cdot}$ etc.
8. $Ka + Ka^{\cdot} \rightarrow Ka - Ka^{\cdot}$
9. $Ka - Ka^{\cdot} + Ka \rightarrow Ka - Ka - Ka^{\cdot}$ etc.

Chain propagation (stages 6, 7, 8 and 9 are crosslinking reactions)

10. $Ka^{\cdot} + Ka^{\cdot} \rightarrow Ka - Ka$ — Chain termination

3. VULCANIZATION (CROSSLINKING) OF RUBBER WITH THE SYSTEM SULPHUR DIOXIDE–HYDROGEN SULPHIDE

1. $KaOOH + SO_2 \rightarrow \begin{Bmatrix} KaOOH \\ SO_2 \end{Bmatrix} \rightarrow KaO^{\cdot} + [SO_2H]^{\cdot}$ — Chain initiation
2. $KaO^{\cdot} + H_2S \rightarrow KaOH + SH^{\cdot}$
3. $Ka + HS^{\cdot} \rightarrow KaSH^{\cdot}$
4. $KaHS^{\cdot} + Ka \rightarrow KaHS - Ka^{\cdot}$
5. $KaHS - Ka^{\cdot} + Ka \rightarrow KaHS - Ka - Ka^{\cdot}$ etc.
6. $Ka + Ka^{\cdot} \rightarrow Ka - Ka^{\cdot}$
7. $Ka - Ka^{\cdot} + Ka \rightarrow Ka - Ka - Ka^{\cdot}$ etc.

Chain propagation (stages 5, 6, 7 and 8 are crosslinking reactions)

8. $Ka^{\cdot} + Ka^{\cdot} \rightarrow Ka - Ka$ — Chain termination

Crosslinking (vulcanization) under the action of dibenzothiazyl disulphide and hydrogen sulphide is the result of reactions 5, 6, 7, 8 and 9 in which crosslinking bonds are formed between the rubber molecules. In reaction 9 this bond is formed by the interaction of two polymeric radicals formed by the abstraction of hydrogen from α-methylene groups in the rubber molecules. This is one of the possible chain termination reactions. In reactions 5 and 6 as also in 7 and 8 the crosslinking bonds are formed by reaction between free radicals and double bonds. Since the quantity of combined sulphur is substantially lower than that corresponding to the number of double bonds lost it is obvious that these radicals result in propagation of a polymerization chain, embracing several rubber molecules.

It is obvious that chain propagation is limited by the steric conditions and high viscosity of the system. According to Dogadkin [8], on vulcanization of solid rubber with dibenzothiazyl disulphide at 143° not more than 2–3 crosslinks are formed for each initiation step. The high viscosity of the system can however be regarded as a favourable crosslinking factor in so far as the polymeric radicals have a longer life in a viscous medium. In so far as the crosslinking effect is observed after reaction with hydrogen sulphide reactions 4, 5 and 6 are obviously more probable.

It is interesting to note that the product of the reaction between benzoyl peroxide and phenyl–β–naphthylamine, O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine (not yet described in the literature), which contains no iminogroup hydrogen atom, is a powerful oxidation inhibitor for rubber (Fig. 10).

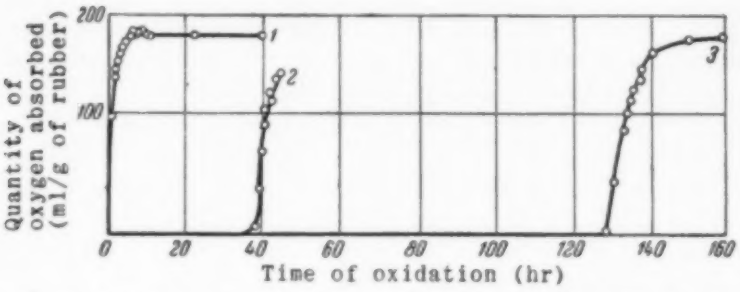

FIG. 10. The kinetics of oxidation of natural rubber at 140° without addition of inhibitor (1), with 1% phenyl–β–naphthylamine (2) and with 1% O–benzoyl–N–phenyl–N–β–naphthylhydroxylamine (3).

This again provides indirect evidence of the radical character of the examples of low-temperature crosslinking (vulcanization) of rubber that we have discussed.

CONCLUSIONS

(1) Elementary sulphur liberated *in statu nascendi* at room temperature by the reactions of dibenzothiazyl disulphide, benzoyl peroxide and sulphur dioxide, with hydrogen sulphide, does not bring about the vulcanization of rubber. In the case of the dibenzothiazyl disulphide–hydrogen sulphide system the addition of 1·2–1·6% of sulphur to a small portion of the rubber was observed, and this does not cause crosslinking. Spectrometric analysis showed that the major part of the rubber (about 90% by weight) remains unchanged. The addition of sulphur to the rubber evidently takes place by an ionic mechanism in this case.

(2) Low-temperature vulcanization (crosslinking) of rubber by the system dibenzothiazyl disulphide–hydrogen sulphide occurs if the rubber solution containing the disulphide has previously been irradiated with diffused daylight or ultraviolet light.

The rate of crosslinking depends on the duration of irradiation and is determined by the reaction between hydrogen sulphide and polymeric rubber radicals resulting from dehydrogenation of the rubber by benzothiazyl radicals formed by photodissociation of the disulphide.

(3) Crosslinking (vulcanization) of rubber by the benzyol peroxide–hydrogen sulphide system takes place in the presence of an amine, for example phenyl–

β-naphthylamine, which is necessary for the formation of free benzoate radicals from the reaction between the peroxide and the amine. The peroxide radicals in this case act in the same way as the benzothiazyl radicals in the dibenzothiazyl disulphide–hydrogen sulphide system.

(4) Low-temperature vulcanization of rubber by the Peachey system (sulphur dioxide–hydrogen sulphide) occurs in the presence of peroxides of the rubber itself. Previous heating of the rubber solution prevents crosslinking.

(5) On vulcanization with the systems dibenzothiazyl disulphide–hydrogen sulphide and benzoyl peroxide–hydrogen sulphide the addition to the rubber of 0·6–0·7% of sulphur takes place, and there is a considerable loss of double bonds, to the extent of 60% of the 1–4 and 75% of the 1–2 bonds.

(6) A radical, chain reaction mechanism has been suggested for the low-temperature crosslinking (vulcanization) of rubber by the systems dibenzothiazyl disulphide–hydrogen sulphide, benzoyl peroxide–hydrogen sulphide and sulphur dioxide–hydrogen sulphide.

(7) The reaction between benzoyl peroxide and phenyl-β-naphthylamine has been studied. A new compound, O–benzoyl–N–phenyl–N–β-naphthylamine, which is a powerful oxidation inhibitor for rubber, has been prepared.

Translated by E. O. PHILLIPS

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HETEROCHAIN POLYESTERS – XVII. POLYESTERS OF PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS*

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(*Received* 25 *January* 1958)

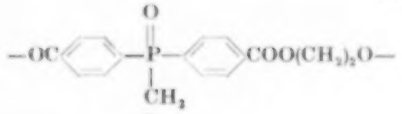
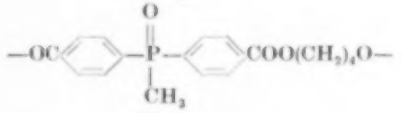
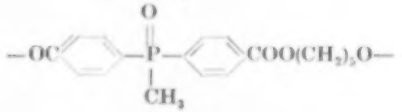
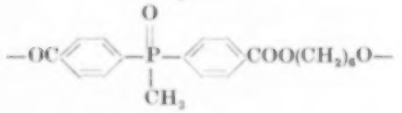
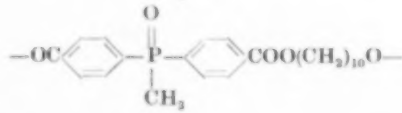
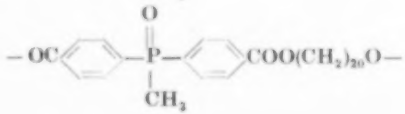
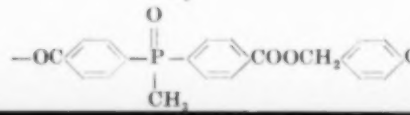
IN a previous report [1] we examined the polyesters of *n*, *n'*–diphenylmethane–, and *n*, *n'*–diphenylketo dicarboxylic acids with aliphatic glycols of varying structure. With the aim of continuing the study of the effect of the structure of the starting materials on the physical properties of the polyesters we obtained polyesters of aromatic dicarboxylic acids containing in their molecule a heteroatom of phosphorus, namely polyesters of oxy–*bis*–(*n*–carboxyphenyl) phenylphosphine and oxy–*bis*–(*n*–carboxyphenyl) methylphosphine. The polyesters which we synthesised were obtained by reaction between the original phosphorus–containing dicarboxylic acid and the glycol, carrying out the polycondensation reaction by fusion first in a nitrogen atmosphere and then in vacuum (residual pressure 1–2 mm).

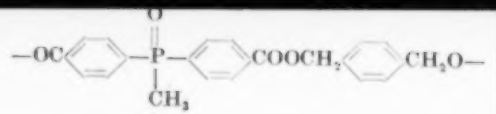
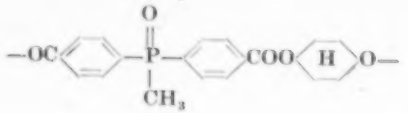
In Table 1(a) data are shown on the polyesters of oxy–*bis*–(*n*–carboxyphenyl) methylphosphine. For these polyesters the constants in the equation relating the number of bonds of the polyester with its molecular weight are not known. Therefore, for a comparative estimate of the molecular weights of the polyesters we determined the molecular weight of one of the samples by the isopiestic method. The molecular weight of the polyester of *bis*–(*n*–carboxyphenyl) methylphosphine with *n*–xylylene glycol, giving a specific viscosity of a 0·5% solution of the polymer in cresol of 0·1, was 15,600. From the data in Table 1 it can be seen that the polyesters of the methyl substituted phosphorus-containing dicarboxylic acid are hard amorphous transparent, somewhat coloured substances. On drawing out from the melt, all of them give long threads. The softening temperatures of the polyesters depend on the structure of the glycol employed. In the series of polyesters of polymethylene glycols of the general formula $HO(CH_2)_nOH$, where $n = 2, 4, 5, 6, 10, 20$, the softening temperature of the polyester drops from 155° for that from ethylene glycol to 60° for that from hexamethylene glycol, rising afterwards to 67° for the polyester from decamethylene glycol and 120° for that from eicosamethylene glycol. Substi-

* Vysokomol. soedin. **1**: No. 3, 357–361, 1959.

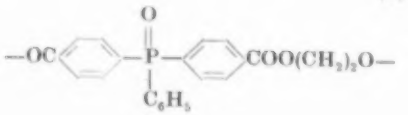
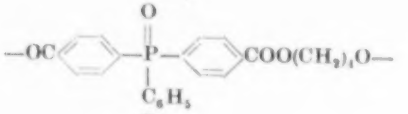
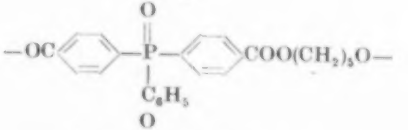
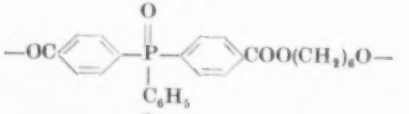
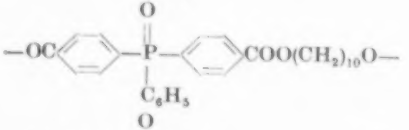
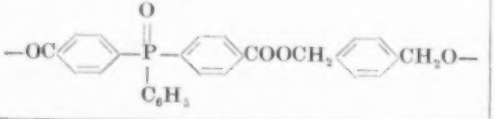
† V. C. Artemova and D. T. Morozova took part in the experimental work.

TABLE 1.

Structural unit of polyester	Softening point °C			Reduced viscosity (η_{sp}/C_c) = 0·5 (in cresol)	Appearance of the polymer and notes
	Determined on a fragment of polymer in a test tube		Determined from thermo-mechanical curve		
	Beginning of deformation	Beginning of thread formation			
(a) Polyesters of oxy–*bis*–(*n*–carboxyphenyl) methyl phosphine					
	145	155–160	—	0·14	Hard transparent brownish colou . On drawing from a melt gives lon threads
	110	127–132	125	0·12	Hard transparent light yellow colour On drawing from a melt gives long threads
	83	93–96	86	0·12	Hard transparent brownish colour. On drawing from a melt gives long threads
	43	60–63	42	0·12	Hard tranparent light yellow colour. On drawing from a melt gives long threads
	56	67–71	52	Does not dissolve	Hard transparent light yellow colour. On drawing from a melt gives long threads
	63	~120	118	Does not dissolve	Hard transparent light brown colour. On drawing from a melt gives long threads
	130	140–145	146	2·2*	Hard transparent light yellow colour. On drawing from a melt gives long threads

	125	140–147	126	0·16	Hard transparent light yellow colour. On drawing from a melt gives long threads
	—	140–145	108	0·12	Hard transparent light yellow colour. On drawing from a melt gives long threads

(b) Polyesters of oxy-*bis* (*n*-carboxyphenyl) phenylphosphine

	165	190–195	—	0·12	Hard transparent light brown colour. On drawing from a melt gives long threads
	130	144–147	129	0·16	Hard transparent light brown colour. On drawing from a melt gives long threads
	108	127–130	105	0·14	Hard transparent light brown colour. On drawing from a melt gives long threads
	73	90–94	79	0·16†	Hard transparent light yellow colour. On drawing from a melt gives long threads
	85	101–104	89	0·14	Hard transparent light yellow colour. On drawing from a melt gives long threads
	—	160–165	140	0·22	Hard transparent light yellow colour. On drawing from a melt gives long threads

* Mol. wt. of polyester determined by isopiestic method = 15,600

† Mol. wt. of polyester determined by isopiestic method = 7000

tution of four methylene groups in the hexamethylene glycol molecule by an aromatic ring is accompanied by an increase in softening point of the polyester. The polyester of *n*–xylylene glycol softens at ~80° above the polyester of hexamethylene glycol. A similar phenomenon is also observed on substitution of three methylene groups in the molecule of pentamethylene glycol with an aromatic ring (polyester of *m*–xylylene glycol).

In Table 1(b) data are shown on the polyesters of oxy–*bis*–(n–carboxyphenyl) phenylphosphine. From these data it can be seen that, like the polyesters shown in Table 1(a), those of the phenyl substituted acid are also solid amorphous transparent substances. When drawn out of a melt they give long threads. The polyester of ethylene glycol has the highest softening temperature. As the methylene chain grows in the original polymethylene glycol (from 2 to 6) the softening temperature of the polyester drops from 190° for the polyester of ethylene glycol to 90° for that of hexamethylene glycol, after which the softening point of the polyester from decamethylene glycol rises to 101°. Substitution of four methylene groups in hexamethylene glycol with an aromatic ring causes the softening point of the polyester (polyester of *n*–xylylene glycol) to rise noticeably.

Comparison of the properties of the corresponding polyesters from the data in Table 1 shows that the polyesters of the phenyl substituted acid have higher melting points than those of the methyl substituted acid. These polyesters, like the others are transparent. Consequently the presence in the original dicarboxylic acid of an atom of phosphorus and side methylene and phenyl substituents gives rise to the formation of a transparent amorphous polymer.

To explain the effect of the $-\overset{\overset{P}{\|}}{\underset{O}{}}(R)-$ group it is helpful to compare with one another the polyesters of phosphorus-containing dicarboxylic acids and the corresponding polyesters of *n*,*n*′–diphenyl methane, and *n*, *n*′–diphenyl keto–dicarboxylic acids, data on which are given in Table 2. From Tables 1 and 2 it can be seen that the polyesters of both phosphorus containing dicarboxylic acids have higher softening points than those of *n*, *n*′–diphenyl methane dicarboxylic acid, notwithstanding the fact some of the polyesters of this acid are characterised by a definite regularity in the disposition of the chains, borne out by their degree of crystallinity. Consequently the substitution of a $-CH_2-$ group between the aromatic rings in the acid molecule by $-\overset{\overset{P}{\|}}{\underset{O}{}}(R)-$, where $R = CH_3-$ or C_6H_5-, is accompanied by an increase in softening point of the polyester, and, clearly, by the disappearance of its crystallinity. The rise in softening point of the polyesters of phosphorus-containing acids can be explained by the higher polarity of the $-P(O)-$ group in comparison with the $-CH_2-$ group, and, as is already known, the presence in the polymer chain of more polar groups leads to an increase in the softening point of the polymers as consequence of the greater inter-chain interaction.

TABLE 2. POLYESTERS OF *n, n'*-DIPHENYLMETHANE and *n, n'*-DIPHENYLKETO-DICARBOXYLIC ACIDS

Glycol from which polyester obtained	Softening point (°C)	Appearance of polyester and its crystallinity
Polyesters of *n, n'*–diphenylmethane dicarboxylic acid		
Ethylene glycol	136	Hard, transparent amorphous
1,4 Butanediol	115	Hard, white, non-transparent, degree of crystallinity ~ 30%
Pentamethylene glycol	37	Hard, semi-transparent, amorphous.
Hexamethylene glycol	80	Hard, white, non-transparent, degree of crystallinity ~ 10%
Decamethylene glycol	92	Hard, white, non-transparent, degree of crystallinity ~ 40%
n–xylylene glycol	189	Hard, non-transparent.
Polyesters of *n, n'*–diphenylketo dicarboxylic acid		
Ethylene glycol	318	Hard, non-transparent, amorphous.
1,4 Butanediol	168	Hard, horny, non-transparent, degree of crystallinity ~ 15%
Pentamethylene glycol	66	Hard, degree of crystallinity ~ 40%
Hexamethylene glycol	123	Hard, non-transparent.
Decamethylene glycol	98	Hard, non-transparent, degree of crystallinity ~ 30%
n–xylylene glycol	203	Hard, degree of crystallinity ~ 15%

The polyesters of *n, n'*–diphenylketo dicarboxylic acid have higher softening points (with the exception of the polyester of pentamethylene glycol) than those of the phosphorus-containing dicarboxylic acid. In this case the drop in softening point can be explained by destruction of the packing density of the polymer chains because of the side substituents at the phosphorus.

In conclusion the authors express their gratitude to V. Kurashev for the phosphorus containing acids.

CONCLUSIONS

(1) Polyesters were synthesised from oxy–*bis*–(*n*–carboxyphenyl) phenylphosphine and oxy–*bis*-(*n*–carbonyphenyl) methylphenyl with glycols of varying structure.

(2) The effect of the structure of the starting materials on the properties of the polyesters was discussed.

Translated by S. C. ALLEN

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CARBOCHAIN POLYMERS AND COPOLYMERS — X. POLYMERIZATION IN BULK OF METHYL METHACRYLATE IN THE PRESENCE OF TRIBUTYLBORON *

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(*Received* 26 *February* 1958)

IT has been established previously by us that tributylboron is a polymerization catalyst for methyl methacrylate in bulk [1] and in solution [2]. To clarify the basic laws of methyl methacrylate polymerization in bulk in the presence of tributylboron we undertook an investigation on the effect of various factors on the course of the polymerization process. The method of carrying out the experiments was as follows. A solution of tributylboron in the methyl methacrylate was used to fill a dilatometer, the volume of which was known for the temperature at which the polymerization was carried out, as well as the volume of a unit of the capillary. The filled dilatometer was put into a thermostat at the given temperature and the changes in the height of the liquid column in the capillary were registered. For calculation of the yield of polymer we used the data [3] of Schulz and Harborth, who determined the volume changes of methyl methacrylate for full conversion to polymer at various temperatures, and showed that there is a direct relationship between the yield of polymer and the decrease in volume. At the end of the experiment the dilatometer was broken, the polymethyl methacrylate dissolved in dichlorethane and reprecipitated by introducing this solution drop by drop into a large volume of methyl alcohol with vigorous agitation. The characteristic viscosity of the reprecipitated polymer was determined at 20°C (solution in dichlorethane). On the basis of the results obtained the velocity constants were calculated for polymerisation of methyl methacrylate as a reaction of the first order.

In the first series of experiments we studied the effect of polymerization temperature on the velocity of the process for constant concentrations of tributylboron (0·10 mol %) on the methyl methacrylate. The results of this series of experiments are given in Table 1.

The mean values of the velocity constants at 30, 40, 50, 60 and 70° are respectively $1{\cdot}14\times10^{-5}$, $3{\cdot}63\times10^{-5}$, $5{\cdot}82\times10^{-5}$, $14{\cdot}8\times10^{-5}$ and $23{\cdot}1\times10^{-5}$ sec^{-1}. The

* Vysokomol. soedin. **1**: No. 3, 362–366, 1959.

TABLE 1. POLIMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF 0·10 MOL.% TRIBUTYLBORON

Duration of reaction (sec)	Yield of polymer (%)	Velocity constant ($K_1 10^5 sec^{-1}$)	Duration of reaction (sec)	Yield of polymer (%)	Velocity constant ($K_1 10^5 sec^{-1}$)
		at 30°C			
2400	2·83	1·19	16,200	15·79	1·06
3600	4·25	1·20	17,700	17·00	1·05
4500	5·67	1·29	19,800	18·41	1·03
5700	7·21	1·32	21,300	19·83	1·04
8100	8·50	1·10	22,500	21·24	1·06
9300	10·04	1·14	23,700	22·66	1·08
10,800	11·33	1·12	24,900	24·08	1·11
12,660	12·75	1·08	26,700	26·91	1·17
13,800	14·16	1·11	33,900	35·45	1·29
		at 40°C			
2400	7·86	3·40	6000	20·22	3·76
3600	11·90	3·52	7200	23·12	3·65
4800	16·81	3·83			
		at 50°C			
900	5·20	5·96	3900	19·69	5·62
1500	8·79	6·11	4500	23·08	5·83
2100	11·64	5·91	5100	25·43	5·75
2700	14·49	5·78	5700	28·45	5·88
3600	17·88	5·48	6300	31·09	5·91
		at 60°C			
600	7·70	13·3	1800	24·59	15·7
900	12·84	15·2	2100	26·30	14·6
1200	17·10	15·6	2400	29·50	14·6
1500	19·25	14·2	2700	33·79	15·3
		at 70°C			
600	12·62	22·4	1500	30·27	24·0
900	19·16	23·7	1800	32·35	21·7
1200	24·69	23·6			

activation energy found from these mean values was 15,500±500 cal/mol, the pre-exponential factor $1·96 \times 10^6$, and the temperature coefficient of the reaction, over the temperature range 30 to 70°, 2.1. To clarify the effect of catalyst concentration on the velocity of polymerization of methyl methacrylate in the presence of tributylboron, two series of experiments were undertaken — one at 30° and the other at 50°. The results of these experiments are given in Tables 2, 3 and partially in Table 1.

TABLE 2. POLYMERIZATION OF METHYL METHACRYLATE AT 30°C IN THE PRESENCE OF TRIBUTYLBORON AT VARIOUS CONCENTRATIONS

Duration of reaction (sec)	Yield of polymer (%)	Velocity constant $K_1 10^5 sec^{-1}$	Duration of reaction (sec)	Yield of polymer (%)	Velocity constant $K_1 10^5 sec^{-1}$
		0·05 mol %			
9000	1·30	0·14	19,800	1·84	0·10
10,800	1·44	0·14	21,600	1·96	0·09
12,600	1·57	0·13	23,400	2·09	0·09
14,400	1·57	0·11	25,200	2·22	0·09
16,200	1·62	0·10	32,400	2·88	0·09
18,000	1·70	0·09	36,000	3·40	0·09
		0·15 mol %			
2400	3·32	1·38	13,200	16·14	1·33
3600	4·74	1·36	14,400	17·81	1·36
4800	6·78	1·47	15,600	19·23	1·37
6000	8·54	1·48	16,800	20·64	1·38
7200	9·10	1·32	18,000	22·53	1·42
8400	11·80	1·50	19,200	24·72	1·48
9600	12·27	1·37	20,400	27·04	1·55
10,800	13·39	1·33			
		0·20 mol %			
1200	2·25	1·90	9600	16·87	1·93
2400	4·51	1·92	12,000	20·06	1·92
3600	6·74	1·93	13,200	22·96	1·98
4800	9·44	2·06	14,400	24·68	1·97
6000	10·82	1·90	15,600	26·44	1·97
7200	13·48	2·02	16,800	29·27	2·06
8400	14·64	1·89			

TABLE 3. POLYMERIZATION OF METHYL METHACRYLATE AT 50°C IN THE PRESENCE OF TRIBUTYLBORON AT VARIOUS CONCENTRATIONS

Duration of reaction (sec)	Yield of polymer (%)	Velocity constant $(K_1 10^4 sec^{-1})$	Duration of reaction (sec)	Yield of polymer (%)	Velocity constant $(K_1 10^4 sec^{-1})$
		0·05 mol %			
1800	7·23	4·17	4800	21·64	5·08
3000	13·38	4·78	6000	25·76	4·97
4200	16·47	4·28	7200	32·99	5·56
		0·15 mol %			
900	7·14	8·24	3600	26·88	8·71
1800	16·89	10·37	4500	38·65	10·9
2700	20·36	8·44			
		0·20 mol %			
600	6·03	10·3	2100	23·91	13·0
900	9·83	11·5	2700	30·22	13·3
1200	13·38	11·9	3000	32·74	13·2
1500	16·18	11·8	3300	35·84	13·5
1800	19·69	12·2	3480	38·65	14·0

The mean values of the velocity constants at 30° and with tributylboron concentrations 0·05, 0·10, 0·15 and 0·20 mol% are $0{\cdot}11\times10^{-5}$, $1{\cdot}14\times10^{-5}$, $1{\cdot}41\times10^{-5}$ and $1{\cdot}96\times10^{-5}$ sec^{-1} respectively. The corresponding mean values for 50° are $4{\cdot}82\times10^{-5}$, $5{\cdot}82\times10^{-5}$, $9{\cdot}30\times10^{-5}$ and $12{\cdot}5\times10^{-5}$ sec^{-1}. The results obtained show that the polymerization velocity constant is directly proportional to the catalyst concentration. In special experiments it was established that the thermal polymerization of methyl methacrylate which may occur at the same time as catalytic polymerization can be neglected since the yield of polymer from purely thermal polymerization at 50°C over 5 hr 40 min was in all 0·84 per cent.

To compare the catalytic activity of tributylboron with that of an initiator such as benzoyl peroxide one can use the data of Schulz and Harboth [3] on methyl methacrylate polymerization at 50°C in the presence of 0·41 mol% (1 wt.%) of benzoyl peroxide, obtained by the dilatometer method: the value of the velocity constant was calculated by us from the data of Schulz and Harboth as for a reaction of the first order. The mean value of the velocity constant for polymerization is $1{\cdot}87\times10^{-5}$ sec^{-1} (see Table 4).

TABLE 4. POLYMERISATION OF METHYL METHACRYLATE AT 50°C IN THE PRESENCE OF 0·41 MOL % BENZOYL PEROXIDE [3]

Duration of reaction (sec)	Yield of polymer (%)	Velocity constant ($K_1 10^5$ sec^{-1})	Duration of reaction (sec)	Yield of polymer (%)	Velocity constant ($K_1 10^5$ sec^{-1})
240	0·54	2·11	2520	4·75	1·94
480	0·77	1·58	2880	5·20	1·86
780	1·49	1·92	3480	6·27	1·87
1200	2·17	1·82	4080	7·27	1·84
1320	2·58	1·94	5280	9·33	1·86
1680	3·03	1·81	5700	10·24	1·89
1920	3·50	1·83	5880	10·38	1·87

Comparison of the velocity constants at 50°C in the presence of tributylboron and benzoyl peroxide show that with a tributylboron concentration of 0·05 mol.% the velocity constant is 2·5 times greater than with a benzoyl peroxide concentration of 0·41 mol% i. e. greater than the concentration of tributylboron by 8 times.

One can deduce that the activity of tributylboron as a methyl methacrylate polymerization catalyst is about 20 times that of benzoyl peroxide as a polymerization initiator.

The characteristic viscosity was determined for the polymers obtained; the determinations were carried out using solutions of the polymer in dichlorethane at 20°C. On the basis of the values for the characteristic viscosity ob-

tained the molecular weights of the polymethyl methacrylate obtained were calculated. The results are shown in Table 5. From the table it can be seen that with increased catalyst concentrations the characteristic viscosity and the molecular weight of the polymethyl methacrylate decreases; a drop in molecular

TABLE 5. CHARACTERISTIC VISCOSITY AND MOLECULAR WEIGHT OF POLYMETHYL METHACRYLATE

Polymerization conditions		η	Molecular weight of the polymethyl methacrylate
Temperature (°C)	Catalyst concentration (mol %)		
30	0·05	14·5	7,000,000
	0·10	7·80	3,200,000
	0·15	5·15	1,900,000
	0·20	1·90	560,000
50	0·05	1·50	400,000
	0·10	1·10	280,000
	0·15	0·80	190,000
30	0·10	7·80	3,200,000
40	0·10	3·12	1,000,000
50	0·10	1·10	280,000
70	0·10	0·50	104,000

weight is also observed with an increase in polymerization temperature with constant catalyst concentration. The molecular weight of the polymethyl methacrylate obtained using tributylboron reaches 7,000,000.

CONCLUSIONS

The kinetics of polymerization of methyl methacrylate in block, in the presence of tributylboron was studied. The influence of temperature of reaction and catalyst concentration on the velocity of polymerization and the molecular weight of the polymethyl methacrylate were clarified.

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CHEMICAL CONVERSION OF POLYMERS—II. POLYOXYETHYLATION OF POLYAMIDES*†

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(*Received* 18 *August* 1948)

ONE of the methods for the synthesis of new high molecular compounds is to convert the macromolecule of the initial polymer into the polymer analogue. This method has been employed for a long time; for instance esters of cellulose, polyvinyl, alcohol and its derivatives etc. Recently chemical conversion of the macromolecules has become widely used for the synthesis of a large number of different polymers with valuable technical properties [1].

The greatest advantage of this method is the possibility of synthesising polymers which could not be obtained directly from monomers by polymerization and polycondensation methods. Especially fruitful is the application of chemical conversion of polymers for introducing into the macromolecule long side chains ("grafts"), of various constitutions and states. This makes it possible to obtain high molecular compounds which combine the properties of two or more parent polymers [2]. This work includes the experiments on formation of hydrophylic polyamides. As is well known the polyamides used in the present day textile industry, along with their big advantages over other types of polymer materials, also possess low hydrophylic properties which greatly limits their application. The data given in the literature on the numerous attempts to give hydrophylic properties to the polyamides amounted, up to recently, to the following: (1) introduction into the polyamide chain of such groups as a simple ester bond, sulphide sulphur, tertiary nitrogen etc. [3]; (2) production of mixed polyamides [4]; (3) production of alkoxymethylpolyamides [5] etc. In all these cases increased solubility was obtained in such solvents as alcohol, and sometimes this even lead to the synthesis of water soluble polyamides. However the polyamides obtained in this manner had low melting temperatures because of the destruction of the regularity of structure and hence they could not be applied for the production of fibres. The most hopeful results for obtaining high melting hydrophylic polyamides were obtained in the synthesis of grafted, polyoxyethylated, polyamides.

* Vysokomol. soedin. **1**: No. 3, 378–386, 1959.

† Report 1 vid. Izv. Akad. Nauk SSSR Otd. Khim. n. 1411, 1957.

Haas and co-workers [6] followed the reaction of polyoxyalkylation of a series of polyamides such as Nylon-66, Nylon-6, mixed and methoxymethylated polyamides and polyamides containing sulphonamide groups in the chain, as well as polyoxyethylation of polyurethanes. As the oxyalkylating agent they used ethylene oxide, propylene oxide, ethylene carbonate and epichlorhydrin, but satisfactory results were obtained with ethylene oxide only.

The polyoxyethylated polyamides produced possessed melting points, crystallinity and solubility differing little from the parent polymers, but they were considerably more elastic and possessed greater permeability than the parent polymers, and the permeability rose with increasing amount of polyethylene oxide introduced into the polyamide. Petukhov and Pakshver [7] obtained polyoxyethylated capron fibres and studied their hydrophylic properties. They found that polyoxyethylenated capron fibres containing ~18% C_2H_4O groups possessed hydrophilicity 33·3% greater than the initial capron.

We have studied the laws of polyoxyethylation of a series of polyamides and the dependance of physico-chemical and mechanical properties of the polyoxyethylated polyamides on the weight increase of polyethylene oxide, the length of the polyethylenated chains and the degree of substitution of the NH-groups.

EXPERIMENTAL PART

The following polyamides were subjected to polyoxyethylation.

(1) Films of polycaprolactam obtained from a continuous production plant where the polymerization process was carried out in the presence of 2% A.G.salt. The films had a thickness of 50–80 μ, a molecular weight, from viscosity, of 18,500, and an equivalent neutralisation of carboxyl groups of 21,000.

(2) Polycaprolactam, synthesised in the laboratory using as stabiliser 2% octadecylamine. The sample had a molecular weight, from viscosity, of 14,000 and an equivalent neutralization of carboxyl groups of 40,000. For the polyoxyethylation this polymer was used as fine rods or powder obtained by reprecipitation by methanol from a cresol solution (see Table 1, reaction 52).

(3) Films of mixed polyamide, Anid G 669, a copolymer of ε-caprolactam, hexamethylene diamine, adipic and azelaic acids [8]. The polyamide was synthesised in glass test-tubes, both without a stabiliser and in the presence of octadecylamine as a stabiliser. The samples had a molecular weight (from viscosity) of 23,000 and 18,500 respectively. The sample obtained with a stabiliser contained no carboxyl groups; that produced without a stabiliser had an equivalent neutralization of carboxyl groups of 6000.

(4) Capron fibres from a plant, both normally oriented and unoriented.

(5) Anid (No. 34) fibres from a plant, normally oriented.

(6) Polyamide fibres from thio-divaleric acid and hexamethylene diamine from an experimental set up, normally oriented and unoriented.

The films, fibres and chip were washed repeatedly (4 or 5 times) with hot water to remove caprolactam and other low molecular impurities and then washed with ethanol (with the exception of Anid G669, which is soluble in alcohol), ether, and dried, first in air, and then in a desicator over P_2O_5 to constant weight.

TABLE 1. POLYOXYETHYLATION OF CAPRON FILMS AND POWDER

Reaction No.	Quantity of C_2H_4O (g/g of the film)	Quantity methanol (g/g of film)	Increase weight polyethylene oxide	N content by Dumas (%)	Polyethylene oxide content from N content (%)	Quantity polyethylene oxide, by Morgan method	Notes
1*	1·8	0·8		11·23; 11·21	9·4	—	
2	0·6	0·3	5·3	—	—	—	
4	2·0	0·9	19·0	—	15·8	12·96	
3	0·8	—	60·6	7·41; 7·28	40·9	—	
5	0·87	—	55·8	8·32; 8·23	33·3	30·8	Not soluble
7	1·13	—	75·2	7·05; 7·18	42·6	33·34	in cresol
8	0·44	—	31·7	9·26; 9·50	24·2	22·0	and alcohols
13	0·93	—	51·0	7·34; 7·39	40·6	—	
14	0·93	—	55·7	8·04; 7·90	35·7	—	
21	2·6	—	98·0	6·38; 6·49	48·1	—	
45	2·0	—	100	5·67; 5·64	54·5	—	
51	2·0	—	98	5·65; 5·70	54·2	44·9	
52†	1·1	—	78·0	6·83; 7·02	43·5	33·4	Soluble in cresol and ethanol

* Reaction carried out at 130 °C.

† Polyoxyethylated capron powder, containing a small quantity of carboxyl groups.

The reaction of the polyamides with ethylene oxide was carried out in sealed ampules. Preliminary experiments showed that the optimum reactions temperature was 80° and the optimum time 15–17 hr. The ethylene oxide was previously purified by passing through a 30% solution of caustic alkali and dried over freshly calcined soda lime. At the end of the reaction the ampules were opened, the reaction products washed, first with ether and then carefully with hot water (Anid G669 with cold water), dried to constant weight over P_2O_5 and subjected to further investigation. The ether and water extracts were evaporated to dryness and the residue analysed. The washed polyoxyehtylated polyamides were estimated for: weight increase of the sample from the polyoxyethylation; the nitrogen content by the Dumas method, the polyethylene oxide content by the Morgan method [9] the average length of side chains and the average degree of substitution of NH–groups. The mean length of polyethylene oxide chains was calculated from the polyethylene oxide content, from nitrogen

analysis and from data from the Morgan method. Also the changes in film dimensions were determined, the swelling in water and 40% alkali, solubility in cresol, methanol, ethanol, acetic acid and water, the viscosity of a cresol solution before and after treatment with alkali and the equilibrium hydrophilicity (at 65% relative humidity).

EXPERIMENTAL RESULTS AND DISCUSSION

The basic part of the investigation was carried out using the reaction between ethylene oxide and capron films. The results of polyoxyethylation of capron films are shown in Table 1.

As can be seen from these data the use of a large excess of ethylene oxide, as a rule leads to films with a large polyethylene oxide, content. Thus, the largest weight increase of polyethylene oxide was obtained in reactions 21, 45 and 51 when 2g of ethylene oxide were used on 1g of film. Methanol reduces the velocity of polyoxyethylation of capron films.

TABLE 2. DIMENSIONAL CHANGES OF CAPRON FILMS AS A RESULT OF POLYOXYETHYLATION

Reaction No.	Weight increase (%)	Dimension of initial film (mm)	Volume (cm^3)	Dimensions of films after reaction (mm)	Volume (cm^3)	Increase in volume (%)
5	55·8	210 × 65 × 0·071	1·0	238 × 75 × 0·0825	1·5	52·5
6	66·0	210 × 82 × 0·0826	1·4	250 × 95 × 0·0956	2·3	59·0
7	75·2	210 × 80 × 0·0737	1·3	253 × 90 × 0·0922	2·1	63·5
8	31·7	210 × 65 × 0·075	1·0	220 × 75 × 0·081	1·3	30·0

On polyoxyethylation of capron films there occurs an increase in all three film dimensions (see Table 2), which suggests that the reaction procedes not only on the surface, but also in the body of the film, although not to the same extent. Apparently the degree of polyoxyethylation on the film surface is greater than inside the film. This is borne out by the fact that hot water washes out of the films a polyoxyethylated product with a considerably greater polyethylene oxide content than in the film itself. Thus, for example, if in the polyoxyethylated film from reaction 1 the nitrogen content is 5·6 per cent (54·2% polyoxyethylene), in the remaining water extract the nitrogen content is 1·46 per cent (88·2% polyethylene oxide). The quantity of material extracted from the films by hot water is 6–17 per cent, as can be seen from the data in Table 3.

At the same time as the polyoxyethylation of the polyamides, there also occurs polymerization of the ethylene oxide. The low molecular polyethylene oxide so formed (m. p. 30–40°C) is easily washed out with ether from the surface

of the film after the reaction. The amount of polyethylene oxide produced was, in the various experiments, 3·5–23%, increasing with increasing excess of ethylene oxide taken into the reaction (see Table 3). In no case was nitrogen found in the residue after evaporation of the ether extract.

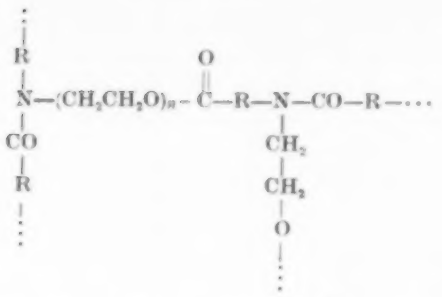
TABLE 3. CHARACTERISTICS OF THE MATERIALS WASHED OUT BY ETHER AND WATER FROM POLYOXYETHYLATED CAPRON FILMS

Reaction No.	Amount C_2H_4O (g/g of film)	Increase in weight from the reaction (%)	Amount of material extracted by ether (%)	Amount of material extracted by water (%)	Nitrogen content in the material extracted by (water)
5	0·87	55·8	6·6	11	—
7	1·13	75·2	7·0	11	—
8	0·44	31·7	3·3	12	—
45	2·0	100	23	6	1·10
51	2·0	98	20	17	1·46

The conduct of the reaction in heterogenous conditions does not give good repeatable results. Thus, for example, under identical conditions in reactions 3 and 5, films were obtained with polyethylene oxide content differing by 10 per cent. The mean degree of polymerization of the polyethylene oxide side chains in a number of cases differed very considerably, although the reaction conditions were the same.

In the polyoxyethylation process of capron films there occurs the formation of a certain amount of cross links, causing the polyamides to partially lose their solubility. The portion soluble in cresol is 39–44 per cent of the weight of the polyoxyethylated polyamide, while the content of the soluble portion rises somewhat with increasing degree of polyoxyethylation. The nitrogen content of the soluble and insoluble portions is the same. The very high swelling of such films in cresol (up to 6000 per cent) supports the view on the small number of cross links.

On treatment with concentrated caustic alkali or hot acetic acid the cross links are destroyed and the polymer becomes soluble. Haas and co-workers [6] also observed that in some cases on polyoxyethylation of polyamides there occurred the formation of cross linkages. They suggested that such cross links are formed from reaction with acetaldehyde, always present to some extent in ethylene oxide. However, addition of acetaldehyde during the reaction of the polyamide samples with ethylene oxide, usually not obtained with a reticulate structure, did not lead to formation of cross links. We think that the formation of cross links may occur because of reaction between the carboxyl end groups and the hydroxyl groups of the polyethylene oxide side chains of the neighbouring molecules:



To test this we carried out the polyoxyethylation of polycaprolactam with an insignificant carboxyl end group content. Grafted polycaprolactam was obtained containing no cross links and easily soluble in cresol and ethyl alcohol (see Table 1, reaction 52). With polyoxyethylation of films of the mixed polyamide Anid G669, containing a considerable amount of carboxyl end groups the formation of cross links was also observed. When carboxyl groups were absent in the initial Anid G669 a product was obtained which was completely soluble in Cresol, alcohol and water (Table 4).

TABLE 4. POLYOXYETHYLATION OF ANID G669

Reaction No.	Equivalent neutralisation of carboxylic groups	Amount of O_2H_4O (g/g of films)	Wt. increase of polyethylene oxide (%)	Solubility
3	6000	2·0	27	Not soluble, swells in water, alcohol and cresol.
5	Traces of carboxyl groups	1·0	22	Soluble in alcohol, cresol and hot water.

In Table 5 data are given in the lengths of the polyethylene oxide side chains and on the degree of substitution of NH–groups in the polyoxyethylated capron films. As can be seen from these data the polyethylene oxide side chains had shorter length when a large excess of ethylene oxide was used or when methanol is added to the reaction mixture, i.e. when better swelling of the polyamide films made the reaction conditions nearer to homogeneity.

Polyoxyethylation of polyamide fibres was carried out in the same conditions as that of the capron films. The results of these experiments are given in Table 6. As can be seen from Table 6 the amount of combined ethylene oxide depends on the degree of orientation of the fibre. For unorientated capron fibre an increase in weight of polyethylene oxide ~ 87 per cent was obtained, while with

oriented capron fibre no increase ~ 37 per cent could be obtained. In the same way in the case of unoriented and oriented fibre from the polyamide of thiodivaleric acid and hexamethylene diamine a weight increase of polyethylene oxide was obtained of 28 per cent and 19 per cent respectively.

The polyoxyethylation of anid fibres procedes very effectively. Even with normally oriented fibre No. 34 the increase reached 68 per cent.

TABLE 5. LENGTH OF POLYETHYLENE OXIDE CHAINS AND DEGREE OF SUBSTITUTION OF GROUPS IN POLYOXYETHYLATED POLYAMIDES

Reaction No.	Amount C_2H_4O (g/g of film)	Polyethylene oxide content (%)	Degree of polymerization of polyethylene oxide chains n	Degree of NH-group substitution (%)
4*	2	15·8	5·6	8·6
8	0·44	24·2	11	7·5
5	0·87	33·3	13·3	9·7
7	1·13	42·6	4·5	43
51	2·0	54·2	5·8	51
52	2·0	43·5	4·3	34

* Reactions carried in presence of methanol.

TABLE 6. POLYOXYETHYLATION OF POLYAMIDE FIBERS

Reaction No.	Polyamide	Quantity C_2H_4O (g/g of fibre)	Wt. increase of polyethylene oxide (%)	N content (%)
29*	Capron	2·2	86·9	6·95; 7·00
30*	,,	1·2	40·0	8·65; 8·43
32	,,	2·2	36·6	9·69; 9·62
19	Anid	0·86	28	10·47; 10·75
37	,,	1·7	34	9·31; 9·04
38	,,	2·3	68	7·62; 7·48
17	From thiodivaleric acid and hexamethylene diamine	0·85	24·5	6·89; 6·96
18*	,,	2·16	28·0	6·75; 7·05

* Fibres unoriented.

PROPERTIES OF POLYOXYETHYLATED POLYAMIDES

Introduction of polyethylene oxide into polyamides, in the form of side chains, changes the crystallinity of the polyamides only insignificantly. From the X-ray photograph shown in Fig. 1 it can be seen that polyoxyethylated polycaprolactam, containing 37·5% polyethylene oxide, has a high degree of cristallinity.

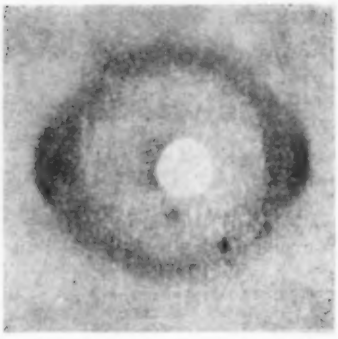


FIG. 1. X-ray Diagram of Polyoxyethylated capron film, containing 37·5% of polyethylene oxide.

The properties connected with the crystalline regions of the polymer (m. p., mechanical properties) change on polyoxyethylation of polyamides equally insignificantly, and to a less amount the less polyethylene oxide is introduced (with the same increase in weight). This is in agreement with Flory's theory, which he put forward for co-polymers [10]. From the thermomechanical curves shown in Fig. 2 it can be seen that polyoxyethylated capron (reaction 4) contain-

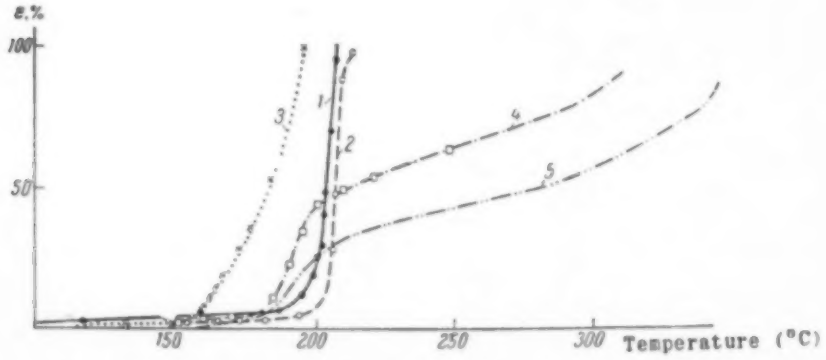


FIG. 2. Thermomechanical curves of compression of capron and polyoxyethylated capron (1) Initial capron (2) Polyoxyethylated capron (reaction 4) (3) Polyoxyethylated capron (reaction 52) (4) Polyoxyethylated capron (reaction 7) (5) Polyoxyethylated capron (reaction 51).

ing 15·8% polyethylene oxide and possessing a degree of NH-group substitutions of 8·6%, melts practically at the same temperature as the initial capron. Sample No. 52, containing 43·5% polyethylene oxide and having a NH-group substitution of 34 per cent melts at 30–40°C below capron. Samples 7 and 51 do not melt even on heating to 300°C, owing to the presence of a considerable number of cross links.

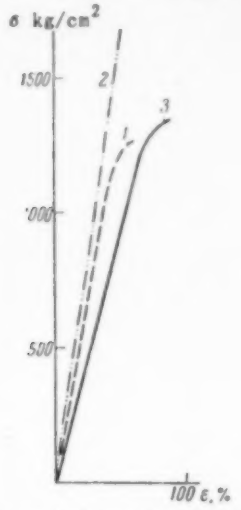


FIG. 3. Dependence of strain on deformation for films from capron and polyoxyethylated capron (parallel to orientation) (1) Initial capron film. (2) Capron film washed with hot water. (3) Polyoxyethylated capron film containing 37·5% polyethylene oxide.

Break elongation and tenacity along the axis of orientation for grafted capron film containing 37·5% polyethylene oxide are only slightly different from the data for the initial film (Fig. 3). On elongation perpendicular to the

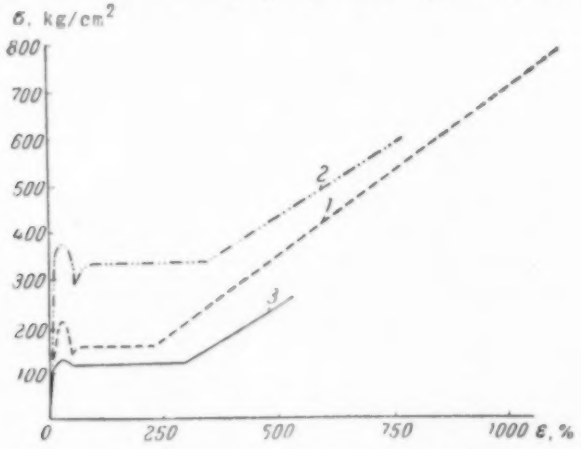


FIG. 4. Dependence of strain on deformation for films from capron and polyoxyethylated capron (perpendicular to orientation) (1) Initial capron film. (2) Capron film washed with hot water. (3) Polyoxyethylated capron film containing 37·5% polyethylene oxide.

orientation axis there is a considerable difference in mechanical properties (Fig. 4) since in the polyoxyethylated film, cross-orientation is difficult because of cross links.

On the other hand, a number of properties change considerably on introduction of polyethylene oxide into the polyamides. For instance the amount of swelling of polyoxyethylated polyamides in water is many times higher than that of the parent polyamides. If the swelling of the initial capron films in water is 7 per cent, then the polyoxyethylated capron films with an increase of 100 per cent of polyethylene oxide swell in water 280 per cent. The water swelling increases with increasing degree of polyoxyethylation, as can be seen from the curve in Fig. 5. When the films are swelled in water their thickness and length perpendicular to the film orientation increase, while along the orientation some shrinkage occurs. The equilibrium hydrophilicity of the polyoxyethylated polyamides (measured at 65% R. H.) is also higher than that of the initial polymers and rises with increasing degree of polyoxyethylation, as can be seen from Fig. 5.

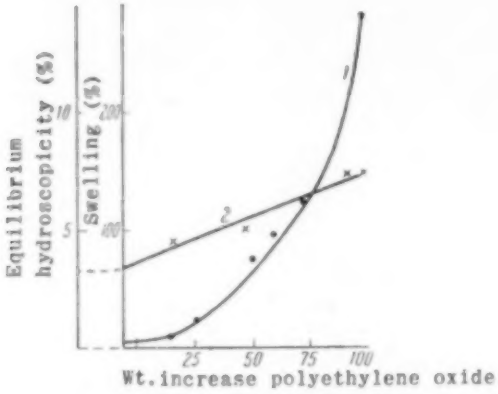


FIG. 5. Dependence of swelling in water and equilibrium hydrophilicity of polyoxyethylated capron films on the wt. increase of polyethylene oxide. (1) Swelling in water; (2) Equilibrium hydrophilicity.

The elasticity of the polyamide films and threads rises sharply. With a large addition of polyethylene oxide the weakly oriented films and threads become rubbery (Table 1, reaction 51 and Table 6, reaction 29).

The solubility of the polyamides changes considerably with introduction of polyethylene oxide in the form of side additions. If the initial capron is not soluble in alcohol the polyoxyethylated product with a polyethylene oxide addition of 68 per cent (not containing cross links) is easily soluble in 70% and 90% ethanol. The initial polyamide Anid G669 is soluble in alcohol but not in water, while the polyoxyethylated product, with 22 per cent addition of polyethylene oxide, is soluble in warm (60°C) water.

The X-ray investigations of polyoxyethylated capron films were carried out in the laboratory of Prof. A. I. Kitaigorodskii, the measurements of mechanical properties in the laboratory of Prof. G. L. Slonimskii. The authors express their gratitude.

CONCLUSIONS

(1) The polyoxyethylation of polyamides was studied using the reaction between ethylene oxide and capron films and powders; capron fibres of various degrees of orientation; Anid fibres; fibres of the polyamide of thiodivaleric acid and hexamethylene diamine of various degrees of orientation; and films of the mixed polyamide Anid G669.

(2) The topochemical reaction of polyoxyethylation of polyamides procedes not only on the surface, but also in the body of the films, threads and powders.

(3) At the same time as the polyoxyethylation of the polyamides there may occur joining of the macromolecules with formation of complex ester bonds from the hydroxyl groups of the side chains and carboxyl end groups.

(4) The swelling of polyoxyethylated capron films in water is many times greater than that of the initial capron films.

(5) The samples of polyoxyethylated capron obtained were very soluble in alcohol and the samples of the mixed polyamide Anid G669 were soluble in water.

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THE DEPENDENCE OF SOLUTION PROPERTIES ON POLYMER STRUCTURE — II. THE APPLICATION OF PRECISION EBULLIOSCOPY IN MOLECULAR WEIGHT DETERMINATIONS OF POLYALUMO-ORGANOSILOXANES*

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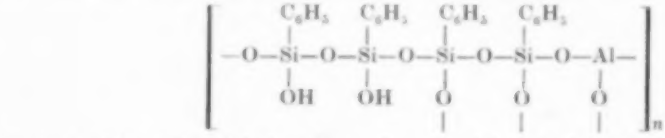
(*Received* 13 *October* 1958)

INTRODUCTION

IN the last ten years a number of authors [1–8] have put forward and tested high sensitivity ebulliometers in which thermo-sensitive elements are used, instead of Beckmann thermometers. In the apparatus proposed by Ray [4], to measure the boiling temperature a sensitive 20 junction copper-constantan differential thermocouple was used. The temperature differences between the boiling solution and its vapour at equilibrium create an e.m.f. in the thermocouple and this is measured by a very sensitive galvanometer. This apparatus gave good results in measurements of molecular weight of polymers between 5000 and 15,000. The sensitivity of the ebulliometer proposed by Ray [4] was enlarged by Smith [3] who worked in conditions of controlled ambient temperature, pressure and humidity. With these precautions Smith measured temperature differences of $1{\cdot}5 \times 10^{-5}$°C which is quite enough for measurement of molecular weight right up to 30,000. Lehrle and Majury [9] selected for the temperature sensitive element a semiconductor (thermister couple) since this had the advantage of being free of electrical side effects characteristic of the thermocouple method. The sensitivity of this apparatus is $(1–2){\cdot}10^{-5}$°C.

For our work we used an ebulliometer of the Ray type [4]. The molecular weights were measured and the viscosity of four fractionated and four unfractionated samples of polyalumo-organosiloxane of structure:



the preparation of which has been described by Andrianov and co-workers [10].

* Vysokomol. soedin. **1**; No. 3, 400–403, 1959.

EXPERIMENTAL

The plan of the ebulliometer is shown in Fig. 1. The working volume is 30 ml. For the temperature measuring equipment a five junction differential thermocouple was used made from Chromel-copel (diameter of each lead 0·4 mm); the thermocouple was made up by the method described by Ray [4]. Inside the ebulliometer a heater was placed made from platinum wire of 0·2 mm diameter. For controlling the constant rate of boiling a voltmeter was connected to the heater. The thermocouple was joined through a shunt with a high sensitivity mirror galvanometer of the M 25/3 type, with a voltage constant of $0{\cdot}35\times10^{-6}$ volts/mm/m. To obviate heat losses into the ambient atmosphere the ebulliometer was put in a glass water jacket (I) connected with an ultrathermostat. Weighed quantities of the substance investigated were introduced through the condenser. To maintain a constant temperature of the condensate the condenser was connected with a 20 litre vessel containing distilled water. Often at the moment when the solvent came to the boil great surface tensions were set up and their dissipation caused the solvent to be thrown up through the condenser. For this reason a spherical bulb (H) was connected to the condenser by a joint ($d=60$ mm), ending in a calcium chloride tube. On changing the voltage fed to the heater the rate of boiling changes and the movement of the galvanometer, related to superheating of the solvent. For this reason it is necessary to work with a constant, previously selected voltage. For selection of the voltage, into the ebulliometer were poured 30 ml of pure solvent and every 20 min the voltage fed to the heater was increased by 0·5 V and measurements made. From the results of the experiments with benzene (Table 1, Fig. 2) it can be seen that the most even boiling is observed at a voltage of 5–6 V. For this reason, when working with benzene a working voltage of 5·5 V was chosen.

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TABLE 1. SELECTION OF WORKING VOLTAGE

Voltage of Voltmeter (reading)	Deflection of scale (mm)	Voltage of Voltmeter (reading)	Deflection on scale (mm)
2·0	Cottrel pump not working	6·0	84·0
		6·5	77·3
3·0	72·0	7·0	77·0
3·5	71·8	7·5	Very vigorous boiling, superheating possible.
4·5	78·5		
5·0	84·7	8·0	
5·5	84·2		

Calibration of the galvanometer scale was carried out for all the solvents used. As standard material carefully purified azobenzene m. p. 68°C, tetratriacontan m. p. 70–73°C and isotetratriacontan m. p. 60–64°C were used. It was found that when working with benzene 1 mm of the scale was equivalent to $3{\cdot}0\times10^{-5}$ °C.

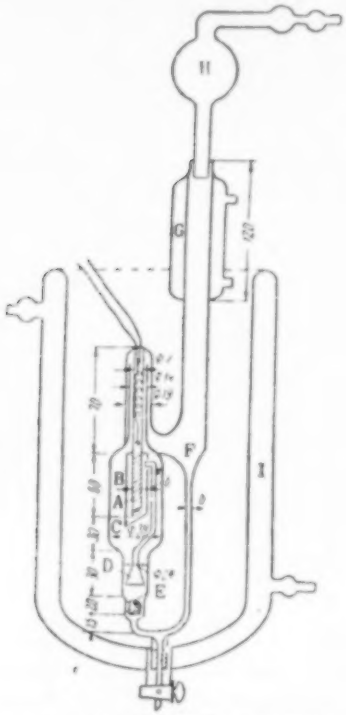

FIG. 1. Plan of ebulliometer. (A) Differential thermocouple (whole length of the pocket), (B) Pocket of thermocouple, (C) Bell, (D) Cottrel pump, (E) Platinum heater, (F) Condensate outlet, (G) Condenser, (H) Bulb, (I) Water jacket.

The benzene (cryoscopic) was purified by 75% H_2SO_4 from traces of thiophene, washed with water to a neutral reaction, dried with $CaCl_2$ and distilled over metallic sodium. K_{eb} (ebullioscopic constant) for benzene was calculated from the Van't Hoff formula as 2·6.

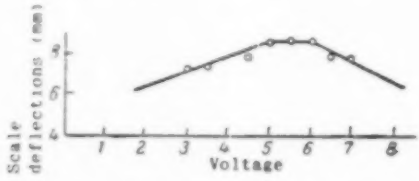

FIG. 2. Graph of dependence of galvanometer deflection on the scale on voltage fed to the heater.

When working with benzene and especially with isopropyl alcohol and methanol, at the beginning of the experiment on the boiling of pure solvent, inequalities in boiling arise from surface tensions in the solvent which distort the readings of the galvanometer.

When using water as the solvent the Cottrel pump does not work owing to the large surface tension of the water. The pump begins to work only after addition of 1–2 portions of the substance under investigation. For this reason the magnitude of the deflections of the galvanometer for pure solvent was found from the point of intersection of the ordinate with the line drawn through the points corresponding to the deflection of the galvanometer at limiting concentrations, as shown in Fig. 3.

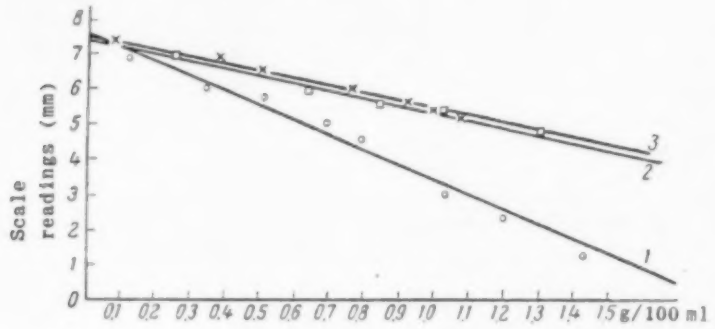

FIG. 3. Finding the magnitude of galvanometer deflections for pure solvent. For 1 and 3 fractions, curves 2 and 3; for unfractionated samples of polyalumoorganosiloxane—curve 1.

The molecular weight of four fractions and four unfractionated samples of polyalumo-organosiloxanes were measured ebullioscopically in benzene. The results are shown in Table 2. The molecular weights were calculated by the method of least mean squares.

TABLE 2. MOLECULAR WEIGHT AND CHARACTERISTIC VISCOSITIES OF POLYALUMO-ORGANOSILOXANES IN BENZENE

Polymer	$[\eta]$	Mn	Polymer	$[\eta]$	Mn
Initial	0·004	5990	4 fraction	0·026	8000
1 fraction	0·018	2550	48** (sample 1)		12,350
2 ,,	0·02	4750	48** (,, 2)		6270
3 ,,	0·034	10,000	48** (,, 3)		7230

* Viscosities measured at 20°C in viscometer with pendant plane.
** Unfractionated polyalumoorganosiloxane.

The authors express their thanks to K. A. Andrianov and E. E. Asnovich for the samples.

CONCLUSIONS

(1) A highly sensitive ebulliometer is described, in which the measuring equipment is a five-junction differential thermocouple.

(2) The possibility of measuring molecular weights of polymers up to 1500 is shown.

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POLYMER ON THE BASIS OF BI*CYCLO*-2,2,1-HEPTADIENE*

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(*Received* 6 *January* 1959)

THE problem of obtaining thermally stable polymers is one of the most important tasks of present day polymer chemistry. Usually, to obtain products capable of withstanding temperatures of 400–500 and even 600°C, metallo-organic polymers, silico-organic compounds and phosphorus containing polymers are used. However, very few pure hydrocarbon polymers are known which possess sufficient thermal stability. Amongst those known are polyphenyls, such as poly-p-xylylene, polyindene resins and some others. Recently there have appeared in the literature indications of the possibility of polymerizing representatives of a new class of monomer-bicyclic hydrocarbons, such as bicycloheptene or norcamphene [1, 2]. In a patent [1] it has been pointed out that polybicycloheptene does not melt right up to its decomposition temperature (300°).

It seemed of interest to study the possibility of polymerizing a bicyclic diene hydrocarbon (bicyclo-2,2,1-heptadiene) and to investigate the properties of the polymer, in particular from the point of view of thermal stability, since by virtue of large intramolecular interaction and stability of structure polybicycloheptadiene should, apparently, possess sufficient thermal stability.

Bicyclo-2,2,1-heptadiene, obtained by a diene synthesis from *cyclo*heptadiene and acetylene [3], may be polymerized using radical polymerization initiators—benzoyl peroxide, cumene hydroperoxide, azo *iso*butyric acid dinitrile, by irradiation with ultraviolet light and X-rays, and also by the use of $TiCl_4$ in dichlorethane as catalyst. All polymerization experiments were carried out with preliminary freezing out and vacuum treatment of the monomer. Polymerization was accompanied by a marked contraction and by the formation of polymer insoluble in its own monomer. The optimum conditions for polymerization appeared to be as follows: 0·1–0·2 per cent of the azo *iso*butyric acid dinitrile; heating for 50hr gradually increasing the temperature up to 200°C. The polymer obtained after removal of low molecular material by extraction with benzene was a slightly yellowish powder, insoluble in the usual organic solvents—heptane, cetane, cyclohexane, naphthalene, tetralin, decalin etc. Polybicycloheptadiene swells slightly in benzene and in its own monomer.

* Vysokomol. soedin. **1**: No. 3, 420–424, 1959.

Investigation of the relationship between deformation and temperature, carried out on a dynamometric balance [4], and also on the frequency apparatus of Aleksandrov [5], showed that right up to 350°C the polymer does not soften and shows no deformation, even under the influence of large stresses, remaining in a vitreous state up to its decomposition temperature. To investigate the thermal stability of polybicycloheptadiene a graph was drawn of the change in weight of a specimen when heated in air (Fig. 1). The measurements were carried out on a recording thermal balance for continuous weighing. From Fig. 1 it can be seen that intensive oxidative destruction of the polymer only begins at a temperature about 400°C and is accompanied by the evolution of gaseous products.

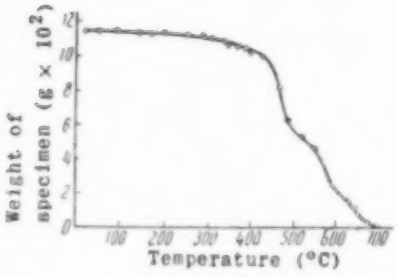

FIG. 1. Change in weight of polybicycloheptadiene on heating.

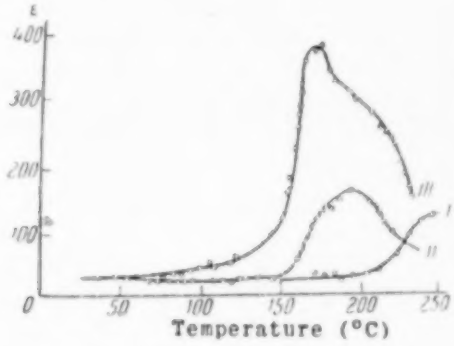

FIG. 2. Relationship between deformation and temperature for plasticised polybicycloheptadiene. (I) 17% plasticiser; (II) 23%; (III) 29%.

In fact darkening of the specimen sets in at temperatures around 300°C, however this does not develop intensively until above 400°C.

Since it was not possible to determine the setting temperature (Tg) of polybicycloheptadiene by the usual methods, since, apparently, it lies above the decomposition temperature, we had to turn to an indirect method of evaluating Tg by introducing plasticisers into the polymer, lowering its softening point. In so far as the depression of the setting temperature of the polymer on introducing a non-polar plasticiser is proportional to the content by weight of the plasticiser [6] it is possible to evaluate Tg for the pure polymer by extrapolating to zero the graph of Tg against plasticiser content. In Fig. 2 are shown three thermo-mechanical curves of the relationship between deformation and temperature for specimens containsing 17, 23, and 29 per cent by weight of plasticiser. As plasticiser was used the hydrocarbon bicyclopentylbutane, which is miscible with the polymer and has a sufficiently high boiling point (130°C/10 mm). From Fig. 2 it can be seen that Tg for the first specimen is 230°C, for the second 160°C, and for the third

130°C. In Fig. 3 is shown the relationship between *Tg* and plasticiser content for specimens of polybicycloheptadiene. Extrapolation to zero plasticiser concentration gives the hypothetical setting temperature of the polymer, lying in the range 360–370°, i.e. absolutely commensurate with its decomposition temperature.

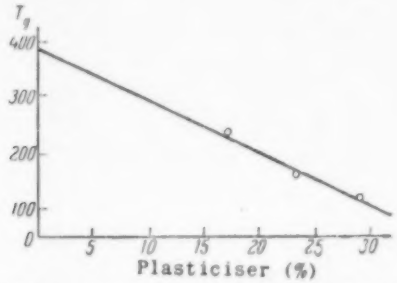

FIG. 3. Relationship between softening point and plasticiser content.

We attempted to arrive at an assesment of the structure of this insoluble and infusible polymer by the use of X-ray analysis and infra-red spectroscopy. From the X-ray data appeared that polybicycloheptadiene has a typically amorphous structure with the absence of any kind of ordered arrangement of the polymer molecules. In view of the insolubility of the polymer and its resistance to deformation it was not possible to obtain an orientated specimen for X-ray analysis. In this connection infra-red absorption spectra of polybicycloheptadiene, bicycloheptadiene and methyl bicycloheptadiene were obtained. The spectra were obtained on a double beam spectrograph of the type IKS-2 using prisms of NaCl and LiF. The specimens of polybicycloheptadiene for exposure were prepared as pastes in petroleum jelly or as discs pressed out of solid solutions of polymer KCl (concentration of polymer 2%).

IR absorption spectra of the three specimens mentioned are given in Fig. 4 (a, b, c). Whilst not dealing with the treatment of absorption bands other than those connected with the carbon-carbon double bond, from Fig. 4a it can be seen that in the spectrum of the monomer bicycloheptadiene there is an strong absorption band at 1542 cm^{-1}, corresponding, according to data in the literature, to vibrations of the carbon-carbon double bond, and a band at 3080 cm^{-1}, connected with the vibration of the hydrogen atoms on the double bond [7]. Analogous absorption bands are also present for methyl bicycloheptadiene Fig. 4b) at 1614 and 3080 cm^{-1}. In this case there is merely added a band at 1376 cm^{-1} corresponding to the vibrations of the methyl group. In the spectrum of polybicycloheptadiene there is also a strong absorption band at 1614 cm^{-1}, corresponding to the vibrations of the carbon-carbon double bond, and a band at 3080 cm^{-1}, connected with the vibrations of the hydrogen atoms on the double bond. In spite of the fact that the concentration of polymer in the specimen of which the spectra were taken was wery low the intensity of the bands connected with the double bond was almost as great as in methyl bicycloheptene.

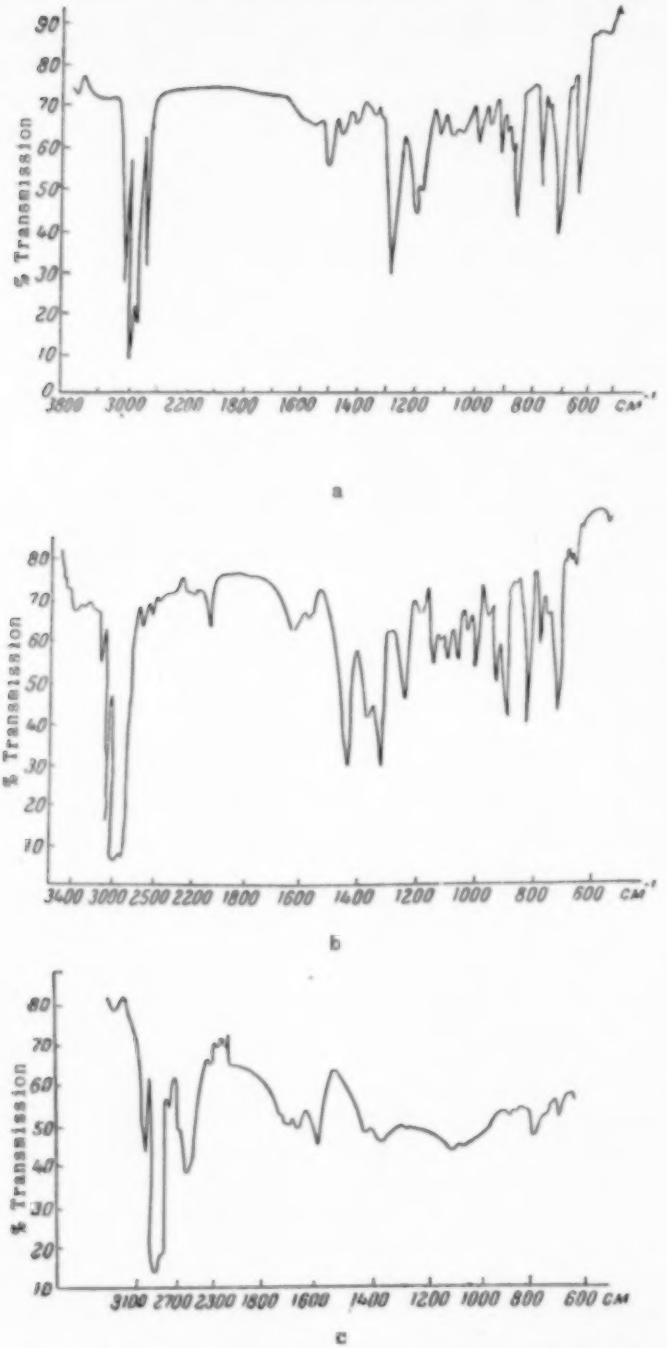

FIG. 4. Infra-red absorption spectra. (a) bicyclo-2,2,1-heptadiene, (b) 5-methyl-bicyclo-2,2,1-heptadiene, (c) polybicyclo-2,2,1-heptadiene.

On the basis of the data obtained the following suggestions may be made as to the structure of polybicycloheptadiene. Polybicycloheptadiene is a polymer with fairly good thermal stability and with chains which are rigid because of the alternation of cyclic residues along the chain. The fact that by IR spectroscopy there has been proved to be present in the polymer a fairly high concentration of double bonds, analogous in character to the double bonds of methyl cycloheptene, indicates that bicycloheptadiene probably polymerises with elimination of the first double bond and retention of the second.

Consequently the formation of a cross-linked structure by means of the second double bond is unlikely, and even if this does take place it is only to a small degree. Also unlikely is the formation of a network through the hydrogen atoms on the tertiary carbon atoms, since in a bicyclic structure these hydrogen atoms have lost their mobility being situated in the bridgehead position of an endomethylene bridge.

The following structure may be put forward for the main bulk of the polymer:

Further investigation is required to give a more accurate picture of the spatial arrangement of the chains and the disposition of the endomethylene bridges. Moreover polybicycloheptadiene probably consists of homogeneous molecular species fairly closely packed together, since the density of the polymer is fairly high (1·138 g/cm³).

CONCLUSIONS

(1) There has been obtained a new polymeric hydrocarbon-polybicyclo-2,2,1,-heptadiene, which has a high thermal stability and does not soften right up to its decomposition temperature (~ 350°C.)

(2) It has been shown that with a suitably selected plasticiser polybicycloheptadiene becomes plastic.

(3) On the basis of thermomechanical and structural investigations a structure has been put forward for polybicycloheptadiene.

(4) The polymer discussed may find application in copolymerization to impart stability to a whole series of specialised polymers.

In conclusion the authors would like to express their thanks to M. A. Salimov for assistance in taking the IR spectra and for discussions on the results.

Translated by A. Holt

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THE SYNTHESIS AND INVESTIGATION OF HYBRID POLYMERS – I. STYRENE AND ISOPRENE BLOCK POLYMERS FORMED BY CATALYTIC POLYMERIZATION IN SOLUTION INDER THE ACTION OF BUTYL LITHIUM*

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(*Received* 23 *January* 1959)

EARLIER [1] it was shown that polymerization of butadiene and isoprene with butyl lithium as catalyst gives practically monodisperse polymers, the molecular weight of which may be governed by the polymerization conditions. A completely controllable polymerization of this kind is possible in two cases: (1) when the reaction terminating the growth of the chains is the formation of high molecular metallo-organic compounds, which are capable of serving as new centres of polymerization, or (2) in the practical absence of any reaction terminating chain growth, i.e. the polymer molecules having commenced growing continue their growth until the whole of the monomer has been used up; it is then possible to ignore side reactions involving impurities whereby active molecules are irreversibly destroyed [2]. Analogous results are given in the work of Szwarc [3], who used the very apt term "living chains". By this means a non-equilibrium molecular weight distribution [3] is obtained, since at any given moment the system being polymerized is a collection of chains which are capable of further growth. If the conditions formulated above are fulfilled and if the process is extended sufficiently the only reason for polydispersity (apart from the usual statistical variation) is if the initiation of all the chains is not simultaneous. However, if the reaction is carried out by adding the monomer continuously to a very well agitated solution of the catalyst it is possible to try and bring out participation in the polymerization reaction of all the catalyst molecules. Moreover, since the number of growing chains remains unchanged and it is possible to add the monomer over a long period of time as is desired (several hours), the initial difference in the length of life of the individual chains rapidly levels out and the breadth of the resulting distribution is merely the ratio of the time needed for initiation to the time of growth, which is determined by the operator. These general considerations are supported by experiment [1].

* Vysokomol. soedin. **1**: No. 3, 443–453, 1959.

The method of living chains described allows, together with the production of a monodisperse product, the production by obvious means of a block polymer with a composition fixed in advance (Szwarc also mentions this). Indeed the termination of the reaction by all the monomer being used up by no means necessitates the "death" of the living chains: by the addition of a fresh portion of monomer the reaction immediately recommences. Consequently, by addition of a monomer of a different kind to the initial polymer chains, growth of new chains of a different composition commences. This process may be easily regulated. After adding a block of the desired length (determined solely by the quantity of the second monomer added) there may be added to the system more of the first monomer—or, if desired, a third—and this process may be carried on as long as desired. In so far as this should give each time a practically monodisperse block, it is easy to see that the method of living chains should, in fact, allow the regulation not only of the chemical composition of the block polymer obtained but also of its fine structure, such as: the number of blocks, the size of each block, the number of blocks of different kinds and the order of arrangement of these blocks. These characteristics distinguish the method of living chains from a number of others as the only method which allows of the production of block polymers with a controlled and regulated composition.

In the present work there is described the production of this kind of block polymer of isoprene and styrene. The communication contains preparative and analytical sections. In general the analysis of block polymers by the usual methods is made difficult because, as a rule, they have a pronounced heterogeneity not only with respect to molecular weight but also according to mechanical composition. In our case neither the one nor the other should appertain, but nevertheless the homogeneity of these block polymers must be proved. It must be further proved that the polymer obtained is a hybrid polymer and not a mechanical mixture of chains of two kinds not bound together. Finally, even if this has been proved, it is necessary to make quite certain that it is in fact a block polymer and not a general statistical copolymer only after all this has been proved can one logically proceed to investigate composition and prove directly the initial assumptions formulated above.

It is this which necessitates the combination of a large number of physicochemical and chemical analytical methods and that is the point of them, as will be clear from the corresponding parts of this communication. First, by turbidometric titration and UV spectroscopy, it is shown that the polymer obtained is not a mechanical mixture of polystyrene and polyisoprene. Further it is shown that the polymer does indeed consist of discrete blocks. For this purpose all the isoprene residues are destroyed by selective oxidation at the double bond. If the residual product obtained (polystyrene) is of a sufficiently high molecular weight this means that these blocks of polystyrene remained after the oxidation, and, consequently, that polyisoprene blocks had been destroyed. If, however, there is

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obtained a low molecular weight product after the oxidation, this will indicate that no block polymer existed. We show below that by oxidation there could indeed be isolated sufficiently large blocks consisting of pure polystyrene. After this we also investigated the quantitative composition of the block polymer; for this we again used UV spectroscopy, and also measured partial specific volumes and determined the refractive index of films. Finally, we determined the molecular weight of the polystyrene blocks and of the block polymer as a whole.

EXPERIMENTAL SECTION

Isoprene was freed from stabiliser, aldehydes, ketones and other impurities by washing with a 10% solution of potassium metabisulphite, 10% caustic soda, distilled water, drying with calcium chloride and caustic soda and distilling through a fractionating column. Immediately before polymerization the isoprene was further dried with metallic sodium and distilled a second time.

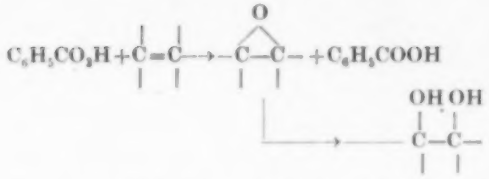
Styrene was purified in the same manner as isoprene. Butyl lithium was obtained by the method of Gilman [4]. Hexane and benzene were freed from saturated compounds with concentrated sulphuric acid, washed with water until neutral, dried with calcium chloride and caustic potash and distilled. Before the polymerization they were further dried with butyl lithium and distilled a second time.

Nitrogen (technical) was freed from oxygen by passing through three columns containing a solution of Cu_2Cl_2 in aqueous ammonia, and dried by passing through columns of solid calcium chloride and caustic potash, concentrated sulphuric acid and a 50% solution of aluminium triethyl in xylene.

The synthesis of a block copolymer. The polymerization was carried out in a well dried system, in an atmosphere of nitrogen, in the absence of oxygen and traces of water.

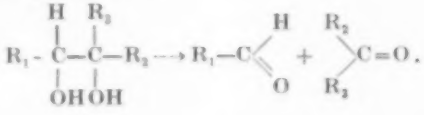
The solvent, hexane or benzene, containing butyl lithium (concentration 0·04–0·05 mol/l), was heated to just below the boiling point of the solvent (66–69° for hexane and 77–80° for benzene). This allowed the polymerization to be roughly followed by the intensity of boiling of the solution. Some isoprene was introduced into the well-stirred solvent catalyst mixture. Polymerization gave first block-polyisoprene. Styrene, the second monomer, was added over 10–15 min after the solution had been brought off the boil. The styrene by combination with the polyisoprene gave the second block. By this means polymers with the desired number of blocks (3,4,5,7, and 9) and containing styrene from 25 to 90% by weight were obtained. The polymer containing 40% styrene and consisting of 9 blocks (5 of which were of isoprene) was investigated in detail.

Oxidation of the block copolymer and isolation of polystyrene. Perbenzoic acid selectively ozidises olefines at the double bond converting them to oxides or glycols (Prilezhayev reaction). The reaction of the polymer with excess perbenzoic acid proceeds according to the following equation:



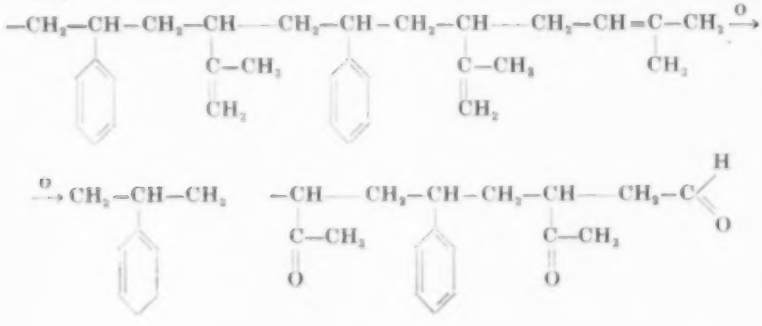
A detailed method for the oxidation of GR-S rubber has been described [5]. We used a simpler method, given for the oxidation of a graft polymer of GR-S and styrene [6]. Two grammes of polymer were dissolved in 200 ml of pure benzene, and 50% excess of perbenzoic acid, calculated on the number of double bonds present, was added : it was assumed that isoprene reacted 100 per cent and that one double bond was present per molecule of isoprene. Simultaneously a blank experiment was carried out using a solution of perbenzoic acid of the same concentration in benzene. The reaction took 24 hr at room temperature. The concentration of perbenzoic acid was determined idiometrically after 18 and 24 hr. In all cases the concentration of acid did not change during the last 6 hr.

The action of perbenzoic acid on polyisoprene blocks leads to the formation of products which contain hydroxyl groups on adjacent carbon atoms. Compounds of this type easily break up under the action of periodic acid, a reagent which is specific for splitting, 1,2-glycols, with the formation of products having carbonyl groups in the terminal positions:



Oxidation of the block polymer of styrene and isoprene gives polystyrene blocks with terminal carbonyl groups, and low molecular weight (aldehydes and ketones) soluble in methyl alcohol.

The polystyrene blocks influence the mode of addition of isoprene units, as a result, of which isoprene has a tendency to add on to polystyrene, in the 1-2, 3-4 positions. When the polystyrene blocks are not sufficiently "pure", i.e. when isoprene units are incorporated in the polystyrene blocks particularly by 1,2 addition, the polystyrene obtained on oxidation may contain several carbonyl groups:



Oxidation of hydrixylated rubber with periodic acid has been described by several authors [6,7]. Some modification of the method was necessary since the molecular weight of our block copolymer is appreciably less than that of the polymers studied in these publications [6,7]. Thus, it was possible to distil the benzene from the solution of the hydroxylated polymer instead of precipitating the polymer with methyl alcohol.

The dried residue was dissolved in dioxan. The calculated quantity of $HIO_4 \cdot 2H_2O$ was dissolved in sufficient water so that, on mixing with the solutiom of the polymer in dioxan, the final concentration of dioxan was ~ 90%. The solution was allowed to stand at room temperature for 24 hr and then heated to 60–70°C for 1 hr. The solvent was distilled off under reduced pressure and the dry residue was washed with a dilute solution of caustic soda and distilled water. The residue was dried, weighed and dissolved in 50–60 ml of methyl ethyl ketone. The polystyrene blocks were precipitated with methyl alcohol and the solution centrifuged (force ~ 10^3g).

Preparation of standard specimens of polyisoprene and polystyrene for turbidometric titratons and spectroscopic investigations. Polystyrene and polyisoprene were prepared by polymerizing the corresponding monomers with butyl lithium in benzene. The polymerization temperature was 80°C, the concentration of calatyst 0·04 mol/l; the concentration of monomer was such that the size of the chains was the same as the size of the corresponding blocks in the block polymer.

ANALYTICAL SECTION

Proof of the hybrid nature of the polymers obtained. In order to show that the polymer obtained was homogeneous nephelometric titrations [8] both of the polymer obtained and the control specimens of polystyrene and polyisoprene were carried out. The experiments were carried out on a special appratus [9] but using, instead of a photoelement, the echelon photometer of Pulfrich [10]. The temperature both of the solution under investigation and of the precipitant were held at 20 ± 0·01°C with a Gepler ultrathermostat. The investigations were carried out in the system toluene (solvent)—ethanol (precipitant). The initial concentration of polymer in the solution did not exceed 0·005 g/100 ml.

Fig. 1 shows typical curves of the turbidity of the system against the quantity of precipitant for specimens of the block copolymer (I), polystyrene (II), polyisoprene (III) and a mechanical mixture of the latter two (IV) (1:1 by weight). As may be seen, the curve for the copolymer (I) has no inflections, which distinguish the titration curve of the mechanical mixture, and lies wholly between curves (II) and (III). Thus is has a composition "intermediate" between that of polystyrene and polyisoprene, and differs in an obvious manner from the curve of the mechanical mixture (IV). This is a proof of the hybrid nature of the polymer obtained and of the relative homogeneity of its chemical composition [8,9,11].

At the same time spectrophotometric investigations of the copolymer, of control specimens of polystyrene and polyisoprene and of the polystyrene obtained by oxidation of the synthetic polymer were carried out on a SF-4 spectrophotometer. The polymers were dissolved in chloroform and their absorption spectra taken relative to the latter. As is known [11] polistyrene selectively absorbs in

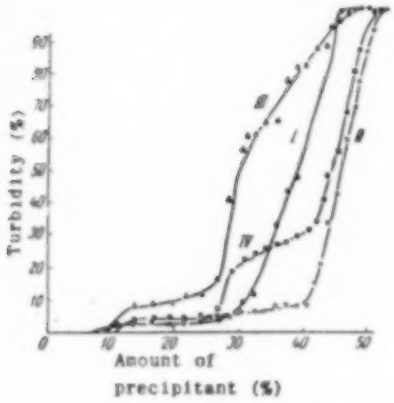


FIG. 1. Nephelometric titration curves. System toluene (solvent) – ethanol (precipitant). (I) Copolymer; (II) Polystyrene control; (III) Poly*iso*prene control; (IV) Mechanical mixture (1 : 1 by weight).

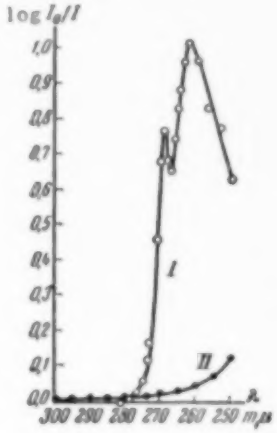


FIG. 2. Absorption spectra of polystyrene (I) and polyisoprene (II) in chloroform ($c = 0{\cdot}5$ g/l).

the ultraviolet with maxima in the region ~ 262 and ~ 269 mμ (in chloroform). (Styrene has its nearest absorption maximum at 282μ [12].) Therefore by measuring the extinction of a polymer which contains polystyrene we can: (1) qualitatively establish its presence in the polymer; (2) determine the content by weight of polystyrene.

Figure 2 shows the absorption spectra of the polystyrene and polyisoprene controls. The spectra were taken at a polymer concentration of 0·05 g/100 ml. As may be seen, whilst polystyrene has a significant absorption in the region 250–280 mμ, polyisoprene absorbs weakly in this region and as a first approximation its absorption may be neglected. From the measurements may be calculated the specific absorption of polystyrene for wavelengths 262 and 269 mμ:

$$\varepsilon = E/c, \tag{1}$$

where $E = \lg I_0/I$ – the extinction, obtained as a reading on the spectrophotometer; c is the concentration of polystyrene, g/l. In our case c = 0·5 g/l; $E_{269} = 0{\cdot}78$; $E_{262} = 1{\cdot}03$, whence $\varepsilon_{269} = 1{\cdot}56$; $\varepsilon_{262} = 2{\cdot}06$.

Figure 3 shows typical absorption spectra of the copolymer (after twice precipitating with methanol) in chloroform at a concentration 0·05 g/100 ml, from which it may be seen that (1) the copolymer has an absorption spectra typical of polystyrene; (2) the magnitude of the absorption (in particular in the regions $\lambda = 262$ and 269 mμ) is lower than for a solution of polystyrene of the same concentration (see Fig. 2) being $\sim 0{\cdot}4$ at a wavelength 269 m and 0·53 at a wavelength 262 mμ.

In conjunction with the results of nephelometric titration this indicates the hybrid nature of the polymer obtained, although it does not constitute sufficient proof that we have a block polymer and not a random copolymer. The following control experiments show the hybrid nature of the polymer in a more direct manner. As is known, polyisoprene is completely insoluble in methyl ethyl ketone, and polystyrene is insoluble in octane. Therefore, by varying the solvent, (selective extraction), followed by spectophotometric analysis it is possible to separate admixed homopolymer (if present) from the supposed block polymer. With this aim the synthesised polymer was dissolved in methyl ethyl ketone and octane and then centrifuged at $1{\cdot}5{\cdot}10^4$ g for 30 min at a concentration ~ 1 g/100ml. After centrifuging the solution methanol was added, the precipitate was carefully broken up and dried to constant weight in vacuum. A solution of it in chloroform was then prepared (concentration 0·05 g/100 ml) and investigated on the spectrophotometer. The results are given in Fig. 4. As may be seen from the figure the spectra of the centrifuged polymer are practically identical with the spectra of the uncentrifuged polymer (see Fig. 3) indicating its homogeneity of composition. On centrifuging only a negligible quantity of substance separated out, on which were carried out the same measurements indicating that a hybrid polymer separated out with a slight preponderance of polyisoprene units (in methyl ethyl ketone) and polystyrene units (in octane).

All the data obtained thus indicate that the great majority of the compound of isoprene and styrene obtained is a heteropolymer, homogeneous in its composition, and that even small quantities of the corresponding homopolymers are absent.

From the absorption spectra given in Fig. 3 it is also possible to determine quantitatively the polystyrene content of the heteropolymer. The concentration by weight of polystyrene in solution equals:

from the absorption at 262 mμ

$$c' = \frac{0{\cdot}53}{2{\cdot}06} = 0{\cdot}257\ g/l$$

from the absorption at 269 mμ:

$$c'' = \frac{0{\cdot}40}{1{\cdot}56} = 0{\cdot}256 g/l.$$

Since the concentration of block polymer in this solution is equal to 0·5 g/l the concentration by weight of polystyrene in the block polymer is 0·257 or (0·256)/0·5≈50%.

Investigation of the nature of the heteropolymer (block or random copolymer?) The results already given do not serve as complete proof that the product is block polymer (by the procedure used in the present work the formation of a graft polymer is excluded [1]). The question is finally decided by analysis of the products remaining after oxidation of the copolymer (the method for which has been described above). The oxidation products were reprecipitated with methanol (twice) and investigated spectrophotometrically. Fig. 5 shows the spectrum of the polymer after oxidation and separation from low molecular weight products. The measurements were carried out at a concentration of 0·5 g/l in chloroform. As may be seen from the spectrum, selective absorption at 262 and 269 mμ exactly corresponds to the absorption of pure polystyrene; in the presence of blocks of poly-

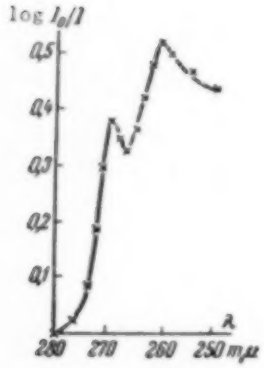


FIG. 3. Absorption spectrum of copolymer in chloroform (c=0·5 g/l).

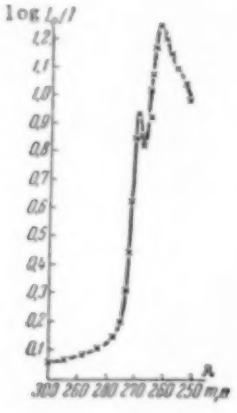


FIG. 4. Absorption spectrum of the centrifuged copolymer in chloroform. I after centrifuging in methyl ethyl ketone; II after centrifuging in octane.

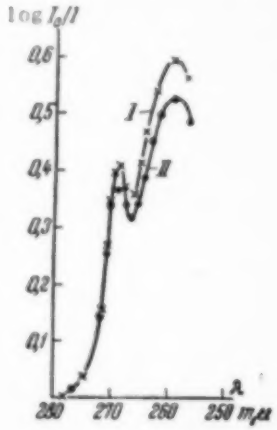


FIG. 5. Absorption spectrum of polystyrene (obtained after oxidation of the copolymer) in chloroform (c=0·5 g/l).

*iso*prene the absorption at these wavelengths would be less (the concentration is the same as for Fig. 2 and 3), since poly*iso*prene has practically no absorption in this region. The presence of some "background" on which the polystyrene absorption is superimposed (and which must be taken into account), is explained by the introduction into the oxidised polystyrene of aldehyde groups for which there is a characteristic maximum in the region 280 mμ [12]. The specific viscosity of this "residual" polystyrene in benzene at 20° is 0·26, which introduces no doubts

regarding its high molecular weight nature. We shall return to the possible meaning of this figure below. Thus we may consider the question about the production of a block polymer as being settled.*

Analysis of the quantitative composition of the block polymer. We give in this section results of determination of composition by other means, possessing, perhaps, even greater general importance, since by no means all polymers selectively absorb in the ultraviolet like polystyrene.

(a) Pynknometric determination of composition. The basis of this method is the additivity of specific volumes, which should apply for mechanical mixtures and block (and also graft) copolymers, but by no means necessarily for random copolymers. The correctness of this rule for mixtures of isotactic and atactic polymers has been shown [13]. We determined partial specific volumes; for this purpose, for block polymer and for control specimens of polystyrene and polyisoprene in toluene we found the relationship:

$$P - P_0 = f(w),$$

where P = weight of polymer solution in pynknometer; P_0 = weight of pure solvent in pynknometer; w = part by weight of polymer.

TABLE 1.

Polymer	v (cm³/g)
Polystyrene	0·91
Polyisoprene	1·12
Block polymer	1·02

At a concentration $< 1\%$ this relationship is linear; therefore from the graph we took the mean value of the quantity $\Delta P/\Delta w$, which was then substituted in the formula for the calculation of partial specific volumes [14]:

$$1 - v\rho_0 = \frac{1-w}{P} \cdot \frac{dw}{dP}.$$

* Further we used a direct qualitative test connected with the production of polymer films from different solvents. In our example the test was carried out as follows. Films were produced by evaporation on mercury of 1% solutions of the block polymer in hexane and methyl ethyl ketone. In the first case was obtained a dull, elastic, completely rubber-like film. In the second case was obtained a transparent, inelastic, almost vitreous film. These differences are occasioned by differences in states of the macromolecules of block polymer during film formation. In hexane the polystyrene blocks are hard clumps which take practically no part in the extra-molecular structure formation of the film, and all its properties are determined in the main by the polyisoprene blocks. On the other hand when films are obtained from methyl ethyl ketone their properties are determined practically solely by the polystyrene blocks. This principle might apparently be applied for the identification of block or graft polymers by hydrodynamic methods. (Note added in proof.)

where ρ_0 = density of the solvent (in our experiments, toluene), v = partial specific volume of the dissolved polymer; P = weight of solution at a proportion by weight of polymer equal to w.

The measurements were carried out in 50 ml pynknometers and on adjusting to the mark they were held at $20 \pm 0{\cdot}05$°C for 1 hr. The results of these experiments are given in Table 1 and Fig. 6.

Further, the following calculation was carried out. Obviously

$$v_{BP} = \Phi_{PI} \cdot v_{PI} + \Phi_{PS} \cdot v_{PS}$$

where v_{BP}, v_{PI} and v_{PS} are the partial, specific volumes of the block copolymer, polyisoprene and polystyrene respectively, and Φ_{PI} and Φ_{PS} are the proportions by volume of polyisoprene and polystyrene in the block polymer, which satisfy the equation

$$\Phi_{PI} + \Phi_{PS} = 1 \tag{4}$$

By substitution we obtain:

$$1{\cdot}02 = \Phi_{PI} \times 1{\cdot}12 + (1 - \Phi_{PI} \cdot 0{\cdot}91)$$

whence, with equation (4), the proportion by volume of polyisoprene and polystyrene in the block polymer are $\Phi_{PI} = 0{\cdot}524$ and $\Phi_{PS} = 0{\cdot}476$.

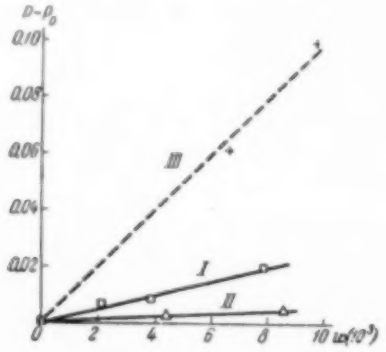


FIG. 6. Relationship between increase in weight of the pyknometer and the proportion by weight of dissolved polymers I copolymer; II polyisoprene; III polystyrene.

The proportions by weight of polystyrene (w_{PS}) and polyisoprene (w_{PI}) are found from the equation:

$$w = \frac{\varphi}{v}, \tag{5}$$

where w = proportion by weight, Φ = proportion by volume, v = partial specific volume. Substituting the corresponding values we obtain: $w_{PI} = \dfrac{0{\cdot}524}{1{\cdot}12} = 0{\cdot}48$ and $w_{PS} = \dfrac{0{\cdot}476}{0{\cdot}91} = 0{\cdot}52$. The results are the same as from the absorption spectra.

It is also possible to calculate the molar proportion m_i of styrene and isoprene in the block polymer, which will be proportional to the proportions by weight and inversely proportional to the molecular weights of styrene and isoprene, and their sum should by definition equal to unity, i.e.

$$m_{\text{isop}} = A\,\frac{w_{\text{PI}}}{68}, \qquad m_{\text{styr}} = A\,\frac{w_{\text{PS}}}{104},$$

and

$$m_{\text{isop}} + m_{\text{styr}} = 1\,; \tag{6}$$

A = coefficient of proportionality.

Substituting w_{PI} and w_{PI} and using equation (6) we find the value of the coefficient of proportionality A. A = 8,2926; the value of the molar proportions $m_{\text{isop}} = 0{\cdot}59$ $m_{\text{styr}} = 0{\cdot}41$.

(b) Refractometric determination of the composition of the block polymer. This method is based on another additivity rule, by which the specific refraction of a mixture equals the sum of the refraction of its components multiplied by the corresponding molar or weight proportions. This method was used by Tsvetkov [15] for analysing a random copolymer.

The specific refraction of the mixture is given by

$$\bar{R} = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} \cdot \frac{1}{\varrho} = \sum_i w_i r_i\,, \tag{7}$$

where

$$r_i = \frac{n_i^2 - 1}{n_i^2 + 2} \cdot \frac{1}{\varrho_i}\,;$$

TABLE 2.

Polymer	n	$\bar{v}$	r
Polystyrene	$1{\cdot}600_0$	0·91	0·399
Polyisoprene	$1{\cdot}519_0$	1·12	0·443
Block polymer	$1{\cdot}549_5$	1·02	0·420

n = refractive index, ϱ = density; the values n and ϱ refer to the mixture, n_i and ϱ_i to the components. Since for polymers $\frac{1}{\varrho_i} = v_i$ [16] we may take

$$r_i = \frac{n_i^2 - 1}{n_i^2 + 2}\bar{v}_i\,. \tag{7a}$$

All necessary data for the calculations are given in Table 2. The refractive index of the corresponding films was measured by daylight on an Abbé refractometer.

Taking the index "1" for polystyrene, and noting that $w_1 + w_2 = 1$, we obtain $0{\cdot}420 = w_1 \cdot 0{\cdot}399 + (1 - w_1)\, 0{\cdot}443$; thus, $w_1 = 0{\cdot}523$, $w_2 = 0{\cdot}477$, agreeing very well with our results quoted above.

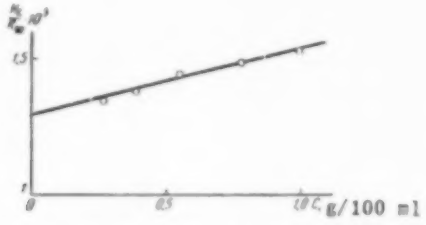


FIG. 7. Scattering of light by a solution of the block copolymer in methyl ethyl ketone.

The molecular weight of the block copolymer was determined by light scattering in the visual polarising nephelometer of Tsvetkov [17], using methyl ethyl ketone as solvent. The specific increment in refractive index of the block polymer equals 0·162 cm³/g ($\lambda = 546$ mμ), which by substitution into the optical constant of Debye gives

$$H = 1{\cdot}826 \times 10^{-6}$$

Figure 7 gives the general form of H_c/R_{90} and c; from which the weight average molecular weight, $M_w = 77{,}000$ and a second virial coefficient for the osmotic resolution, $A_2 = 1 \cdot 2 \cdot 10^{-4}$ cm³/g².

Obviously the weight average molecular weight of five isoprene blocks should equal approximately 38,000 and the weight of each block 1600. As for the styrene blocks, their molecular weight should be ~ 10,000. This figure is somewhat incompatible with the value for the specific viscosity, which equals 0·26 (see above) and corresponds to a molecular weight approximately three times greater. However, perhaps too great importance should not be attached to this figure, since during the oxidation there may take place both a partial combination of the polystyrene molecules and some change on their configuration and interaction through the appearance of carbonyl groups. Therefore the increased viscosity of the polystyrene residue after oxidation should be considered rather as a sign that some such change has taken place than as a measure of the molecular weight of the initial polystyrene blocks.

CONCLUSIONS

The foregoing analyses show that the method of living chains permits the production of a block copolymer near to the desired composition. Because of the lack of data we cannot pursue in detail the reasons why the content by weight and by molecules of styrene turned out to be approximately 10 per cent higher than that

expected. We can only note that, of necessity, when a polymerization is carried out in practice there is some small measure of deviation from the "ideal" conditions formulated in our paper.

Two of the most obvious deviations from ideality are as follows:

(1) On each addition of monomer some fraction of the chains are terminated (i.e. "die") because of inconsidered impurities. Apart from reducing the number of blocks these impurities lead to an increase in the polydisperseness of the blocks themselves [1,3]. (Source of polydisperseness of dimensions.)

(2) As has been shown by one of us [2], the completeness of utilisation of styrene and isoprene is by no means identical, being significantly greater in the case of the former. Because of the incompleteness of conversion of isoprene in the early stages in the growth of each polystyrene block (i.e. immediately after the addition of a new portion of monomer) there may be formed relatively short "aggregations" with a change in compositions of the chains. It must also be borne in mind that the speed of growth of the styrene blocks is significantly greater than the speed of growth of the isoprene blocks, and therefore with an identical degree of purity the impurities in the monomer will exert a greater influence on the growth of the isoprene chains. Therefore during the growth of the styrene blocks there is always some quantity of isoprene present, which is incorporated in these blocks with the formation of 1–2 and 3–4 links and causes inhomogeneity within the blocks. For this reason there arises, as was noted earlier, the "aldehyde" background on measuring the UV absorption of the polystyrene remaining after oxidation. (Source of polydisperseness in composition.)

Finally, there must be taken into account the possible losses of isoprene as the more volatile monomer, since the system is not completely sealed and the polymerization temperature is high. The maximum losses of isoprene would apparently be by the growth of the last block, since the remaining unused isoprene could not be incorporated in a new polystyrene block. Thus, the excess of styrene in the block polymer compared with the concentration used can be explained in the last analysis by the more complete utilisation of styrene, and this result can be considered as an experimental fact.

The other side of the question seems to us to be more substantial. From the analytical section it follows that after the block nature of the heteropolymer has been proved there is no further difficulty in an accurate determination of its composition, which can be carried out by various physical methods. The simplest of these is, perhaps, the refractometric in conjunction with determination of the "dry" density of the polymer.

In conclusion we will mention one possible method of investigation which could not be used in the present case because of the low molecular weight of the block polymer. We have in mind equilibrium sedimentation in a medium of graded density [18]. This may be accomplished by using as solvent a mixture, let us say, of chloroform and benzene, the densities of which differ by 0·7. After establishing a constant gradient (in the field of an ultracentrifuge) components with different

specific volumes should take up definite positions in the cell of the centrifuge, i.e. they should cease to move upwards or downwards, having reached the point where the density of the solvent equals their own densities. With a mechanical mixture the dissolved polymer will concentrate around two poles, whilst a hetero- (block or graft) copolymer should take up an intermediate position and spreading to the corresponding poles might appear as a relative measure of polydisperseness in composition or size. We intend to return to this question in the future.

The physical methods of investigating the composition of the heteropolymer described in the analytical section can be recommended for wide application.

Translated by A. HOLT

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* VOL. 1, No. 1, 1959*

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A STUDY OF THE DIELECTRIC LOSSES AND DIELECTRIC CONSTANTS OF CRYSTALLIZING POLYMERS

G. P. Michailov and B. I. Sazhin, Vysokomol. soedin. 1: No. 1, 9-16, 1959.

In the report have been presented the results of studies of the dielectric losses of natural rubber, polyethylene, polyethyleneterephthalate, polytrifluorochlorethylene and a number of other polymers of different degrees of crystallinity. It has been shown that crystallization of the polymers is accompanied by a decrease in dielectric losses of a relaxation character. In addition, for one type of loss, associated with the segmental heat motion on the amorphous regions, the relaxation time increases on crystallization.

STUDIES IN THE MOLECULAR STRUCTURE OF SYNTHETIC FIBRES—XIII. POLYENANTHAMIDE

E. Z. Fainberg, V. O. Gorbacheva and N. V. Mikhailov, Vysokomol. soedin. 1: No. 1, 17–20, 1959.

An X-ray and thermochemical study has been made of polyenanthamide. The data obtained have been compared with the corresponding results for polycapramide. Polyenanthamide has been shown to crystallize easier than the latter. In the process orientation of the enanth fibres the crystals have been shown to increase in size.

THE EFFECT OF THE MOLECULAR WEIGHT OF SOME VITREOUS POLYMERS ON THEIR INTEGRAL HEATS OF SOLUTION

A. A. Tager, Vysokomol. soedin. 1: No. 1, 21–28, 1959.

In the study the integral heats of solution of vitreous polymers have been determined over a wide range of molecular weights. There homologous series of polymers have been investigated, namely, polystyrenes, polymethylmethacrylates and triacetylcelluloses. The results of the study showed an increase in the positive values of the heats of solution with increase in degree of polymerization. This is especially well expressed in the homologus series of polystyrene polymers. The relationship is explained by a value considerably less than equilibrium for the chain packing density of the higher molecular homologues due to the large relaxation times in the vitrification of a number of polymers. With the low molecular members the packing density is close to the equilibrium value. Hence, as the molecular weight of the polymer increases, there is an increase in the looseness of its packing; the interaction energy between the chains diminishes, and, consequently, the heats of solution increase.

* English abstracts reprinted from Vysokomol. soedin. 1: No. 1, 1959.

A STUDY OF THE EFFECT OF POLYMER CRYSTALLIZATION ON THE DIELECTRIC LOSSES

G. P. Michailov and B. I. Sazhin, Vysokomol. soedin. 1: No. 1, 29–35, 1959.

THE dielectric constants and tangents of the angle of the dielectric losses have been determined for 12 crystallizing polymers over a wide range of frequencies and temperatures. For the major part of the polymers two types of dielectric losses of a relaxation nature have been revealed, reflecting different types of thermal motion.

EFFECT OF SHAPE OF THE MOLECULAR CHAINS ON THE PROPERTIES OF SOLUTIONS AND VULCANIZED FILMS OF BUTYL RUBBER

T. V. Dorokhina, A. S. Novikov and P. I. Zubov, Vysokomol. soedin. 1: No. 1, 36–45, 1959.

THE properties of solutions of fractionated butyl rubber in thermodynamically 'good' (CCl_4) and thermodynamically 'poor' (C_6H_6) solvents have been studied at different temperatures with the aid of viscometric and osmometric methods.

Based on calculation of the thermodynamic functions and the mean molecular sizes it has been found that at $t = 25°$ C in the good solvent (CCl_4) the butyl rubber polymer chains are in a relatively straightened out condition, whereas in the poor solvent (C_6H_6) they are coiled up.

The effect of the type of solvent on the configuration of butyl rubber chains has been utilized in the production of films with a given initial polymer configuration.

Vulcanizates obtained from CCl_4 solutions of the rubber mixture with straighter chains considerably excel in strength and relative elongation those obtained from mixtures dissolved in C_6H_6 and possessing a more coiled shape.

The initial configuration of the polymer chains has an important influence on the relaxation processes and on the kinetics of swelling of butyl rubber vulcanizates.

THE EFFECT OF CHEMICAL NATURE OF SOLVENTS ON THE OXIDATION OF RUBBER IN SOLUTIONS

T. G. Degteva and A. S. Kuzminskii, Vysokomol. soedin. 1: No. 1, 73–83, 1959.

THE effect of the chemical nature of solvents on the oxidation of rubber solutions has been investigated. It has been shown that the oxidation rate increases in the order: benzene < toluene < xylene < ethylbenzene < isopropylbenzene < tetralene. The solvents have been found to take part in the development of a radical chain mechanism of rubber oxidation. The more labile the hydrogen atom in the solvent molecule, the easier the chain propagation reaction and the greater the oxidation rate. Benzene has been shown to add OH radicals formed during the rubber oxidation process, with the production of phenol. The kinetics of phenol accumulation have been followed in the oxidation of a 4% rubber solution in benzene at 110° C.

PHASE EQUILIBRIUM IN THE TERNARY SYSTEM: POLYMER-TWO LOW MOLECULAR LIQUIDS

S. P. Papkov, Vysokomol. soedin. 1: No. 1, 84–87, 1959.

THE types of equilibrium diagrams in the ternary system: polymer-two low molecular liquids have been examined. As examples, the experimental study has been presented of the

systems: cellulose nitrate-acetone-water and cellulose diacetate-chloroform-ethyl alcohol. These systems are characterized by the formation of two homogeneous liquid phases. Complete phase equilibrium is rapidly established owing to the relatively low viscosity of both phases.

THE EFFECT OF TEMPERATURE ON THE VISCOSITY OF CONCENTRATED SOLUTIONS OF POLYMETHACRYLIC ACID AND ITS SALTS

Yu. S. Lipatov and P. I. Zubov, Vysokomol soedin. 1: No. 1, 88-93, 1959.

THE temperature dependence of the specific viscosity of aqueous solutions of polymethacrylic acid and its sodium salts has been investigated over the range of concentrations 0·5-8% and of temperatures 20–60°. The fundamental correlations for the change in specific viscosity with the degree of neutralization of the polyacid established for dilute solutions hold up to a concentration of 6%. For solutions with degree of neutralization of the polyacid up to 15% a decrease in the specific viscosity is observed with rise in temperature, whereas for those with degree of neutralization 25 and 40% the specific viscosity increases with the temperature the increase being the more rapid the higher the solution concentration. A sharp increase in absolute viscosity of the 8% solution with rise in temperature has been found.

ON THE MECHANISM OF HARDENING OF EPOXIDE RESINS BY AMINES

L. I. Golubenkova, B. M. Kovarskaia, I. I. Levantovskaia and M. S. Akutin, Vysokomol. soedin. 1: No. 1, 103–108, 1958.

THE interaction of epoxide resins with amines of both the aromatic and aliphatic series has been studied with the aid of thermomechanical and infra-red spectroscopic methods.

It has been shown that as a result of the interaction both secondary and tertiary amines are formed. The process of development of tri-dimensional structures in epoxide resins is associated with the formation of tertiary amines, the content of which determines the rigidity of the structures.

THERMOMECHANICAL INVESTIGATION OF EPOXIDE RESINS

L. I. Golubenkova, B. M. Kovarskaia and M. S. Akutin, Vysokomol. soedin. 1: No. 1, 109–113, 1959.

THE process of hardening of epoxide resins of varying molecular weight by the action of dicarboxylic acid anhydrides (phthalic and maleic) has been investigated.

It has been shown that epoxide resins hardened by these anhydrides are characterized by high heat stability (250° C), considerably exceeding that for resins hardened by amines. The rate of hardening of epoxide resins by maleic anhydride is much greater than by phthalic anhydride. The products hardened by the former are less elastic at higher temperatures and less fragile at room temperatures than those hardened by the latter.

THE SYNTHESIS OF STARCH AND STYRENE GRAFT COPOLYMERS AND A STUDY OF THEIR PROPERTIES

V. A. Kargin, P. V. Kozlov, N. A. Platé and I. I. Konoreva, Vysoiomol. soedin. 1: No. 1, 114–122, 1959.

ON ozonating aqueous starch suspensions, active peroxide groups are formed on the starch which have been used for initiating styrene polymerization and for the production of starch and styrene graft copolymers. The length of the grafted-on chains of polystyrene is commen-

surate with that of homopolystyrene, a side product of the reaction. The starch-styrene graft copolymers with different component ratios may under certain circumstances be good emulsifiers for water-oil emulsions.

It has been established thermomechanically that for all graft copolymers with up to 60% starch content the vitrification temperature remains constant and coincides with that for the pure polystyrene. At the same time these products do not give rise to flow, owing to the rigid structure of the starch. On these specimens the principle has again been confirmed that the properties of graft copolymers are additive with respect to the properties of the initial components.

An interpretation has been suggested of the mechanism of the homopolymerization of styrene inside the starch granules, leading to the formation of strained structures with higher vitrification temperatures than the pure graft copolymers.

MEASUREMENT OF THE BIREFRINGENCE OF POLYETHYLENETEREPHTHALATE FILMS

G. L. Berestneva and P. V. Kozlov, Vysokomol. soedin. 1: No. 1, 126-127, 1959.

A METHOD is proposed for measuring the anisotropy of films and fibres from polyethyleneterephthalate with the aid of terylene compensators.

ON THE STRUCTURE OF SOLID SOLUTIONS OF *n*-PARAFFINS

A. I. Kitaigorodskii, and Yu. V. Mnyukh, Vysokomol. soedin. 1: No. 1, 128–131, 1959.

THE dependence of d_{001} on the mixture composition of the binary *n*-paraffin system C_{30}-C_{24} and C_{29}-C_{28} has been investigated by means of x-ray photography, using a low-angle camera. The character of the relation indicates the existence of two different mechanisms for the formation of the solid solutions, one corresponding to the case when the component with longer aliphatic chain is the 'solvent' and the other to the reverse. The distortion of plane-zigzag form of the chain was found to take place in the field of terminal groups in solid solution of *n*-paraffins.

INDICATRIX FOR THE LIGHT SCATTERING OF POLYMER SOLUTIONS AND VOLUME EFFECTS

V. E. Eskin, Vysokomol. soedin. 1: No. 1, 138–142, 1959.

A DEVIATION of the angle distribution curve for the light scattering of solutions from the shape of the Debye plot has been found in the case of high molecular polystyrene in toluene. This is discussed in light of the theory in which account is made of the volume effects on the light scattering of polymer solutions and in connection with the problem of obtaining exact data on the sizes of macromolecular clusters.

A STUDY OF THE MOLECULAR STRUCTURE OF STEREOREGULAR POLYMERS —I. ISOTACTIC POLYPROPYLENE

N. V. Mikhailov, E. S. Fainberg and V. O. Gorbacheva, Vysokomol. soedin. 1: No. 1, 143–148, 1959.

X-RAY analysis and heat capacity determinations have been carried out of polypropylene and of the fractions isolated from it, and the viscosities of their dilute solutions have been measured.

It has been shown on isotactic polypropylene as example that regularity in the chemical structure of the molecular chain is a requisite, but not a sufficient condition for crystallization of a polymer.

Analysis of the results of heat capacity measurements on polypropylene has led to the conclusion that the heptane fraction of polypropylene has a plasticizing effect on isotactic polypropylene. From this it may be concluded that in order to increase the elasticity of fibres obtained from isotactic polypropylene the initial polymer should contain some of the heptane fraction.

Based on the experimental data it has been suggested that the heptane fraction has a complicated structure and is homoblock-polymer.

FORMATION OF GRAFT POLYMERS BY THE OZONATION OF CELLULOSE

V. A. Kargin, Kh. U. Usmanov and B. I. Aikhodzaev, Vysokomol. soedin. 1: No. 1, 149–151, 1959.

In the report a method is described for the production of cellulose graft polymers by means of polyperoxide compounds of cellulose.

The authors have found the conditions for the formation of active polyradicals from cellulose peroxides and have obtained graft copolymers of the latter with styrene (6·6% polystyrene by weight) and acrylnitrile (21% polyacrylnitrite by weight). The grafting of styrene to viscose cord increases its adhesion to rubber.

HIGH MOLECULAR POLYMERS OF ETHYLENE OBTAINED WITH THE AID OF MIXTURES OF ORGANOLITHIUM COMPOUNDS WITH TITANIUM TETRACHLORIDE

K. A. Kocheshkov, V. A. Kargin, T. V. Talalaeva, T. I. Sogolova and O. A. Paleyev, Vysokomol. soedin. 1: No. 1, 152–156, 1959.

A study has been made of the polymerization at normal pressure of ethylene in the presence of 13 organolithium compounds mixed with titanium tetrachloride in a 1:1 ratio, *n*-hexane being used as solvent. The catalysts were of varying activity, allowing the polymerization to be carried out within the limits of −20 to 60° C.

With the aid of X-ray analysis and infra-red spectra measurements it has been established that the polyethylenes obtained are highly crystalline, with very little chain branching, no significant difference in the degree of branching being observed between them.

The molecular weight of the polymers is of the order of 300,000 and the density 0·97 g/cm³.

Employing a thermomechanical method it has been shown that the ethylene polymers possess high yield and tensile strength values and a softening temperature of 135–140° C. Uncommonly high irreversible elongation values were obtained for some specimens: *n*-$C_{12}H_{15}$Li - 2000%, *n*-C_5H_{11}Li - 2200%, *n*-$CH_3C_6H_4$Li > 2200%. The difference in the mechanical properties of the polymers leads to the inference that their structure depends upon the nature of the organometallic catalyst radical.

DEVELOPMENT OF METHODS FOR THE SYNTHESIS OF CELLULOSE ESTERS WITH N-SUBSTITUTED AMINO ACIDS

Lin'-Yan', V. A. Derevitskaia and Z. A. Rogovin, Vysokomol. soedin. 1: No. 1, 157–161, 1959.

The following cellulose esters with N-substituted amino acids have been obtained by the action of the acyl chlorides of N-substituted amino acids on inclusion of cellulose in a solvent medium: N-carbobenzoxy- and N-phthalylglycine, and N-carbobenzoxyaminoenanthic and N-phthalylaminoenanthic acids. The esters were of a degree of substitution from $\gamma = 20$ to 162.

ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* VOL. 1, No. 2, 1959 *

ON THE PART PLAYED BY MOLECULAR INTERACTION IN THE HYDROLYSIS OF POLYSACCHARIDES IN A HETEROGENEOUS MEDIUM

A. A. Konkin and Z. A. Rogovin, Vysokomol. soedin. 1: No. 2, 177–181, 1959.

THIS paper is devoted to an elucidation of the effect of the intensity of molecular interaction on the rate of hydrolysis of polysaccharides in a heterogeneous medium. In line with this objective the relative intensity of molecular interaction of the polysaccharides was determined and the results were compared with the values for the rate constant of hydrolysis of the polysaccharides in the medium. The relative intensity of molecular interaction of the polysaccharides was obtained from their heats of swelling and water-vapour sorption. The studies were made on hydrate cellulose, amylose, agar-agar, mannan, galactan, laminarin and xylan. A direct correlation was found to exist between the hydrolysis rate of the polysaccharides in a heterogeneous medium and the intensity of molecular interaction. With increase in the latter, there is a fall in the rate of hydrolytic rupture of the acetal bond of the polysaccharides.

STRUCTURATION PROCESSES IN SOLUTIONS OF HYDROCARBON AND OF POLYACRYLATE POLYMERS

V. A. Kargin, N. F. Bakeev and V. B. Ryzhov, Vysokomol. soedin. 1: No. 2, 182–184, 1959.

MIXTURES of water soluble compatible polymers have been studied with the aid of an electron microscope method. To elucidate the character of the interaction of polymer chains possessing different configurations, the mixtures selected for the investigation comprised globular starch, water soluble fibrillar oxyethylcellulose and polyacrylates both of the globular and of the ultimately extended shape. Of the mixtures, only the polymers with extended chains interact. No interpenetration and reaction occurs when one of the chains has a globular configuration.

STUDIES ON THE MOLECULAR STRUCTURE OF SYNTHETIC FIBRES—XIV. PHYSICO-CHEMICAL AND PHYSICO-MECHANICAL PROPERTIES IN THE SERIES OF POLYCAPRAMIDE-POLYUNDECANAMIDE POLYAMIDES

N. V. Mikhailov, T. I. Shein, V. O. Gorbacheva and V. N. Topchibasheva, Vysokomol. soedin. 1: No. 2, 185–190, 1959.

A COMPARATIVE investigation has been made into the structure, physico-chemical and physico-mechanical properties of polyamides of the series polycapramide-polyundecanamide.

* English abstracts reprinted from Vysokomol. soedin. 1: No. 2, 1959.

It has been shown that with increase in the number of methylene groups in the elementary unit of the polyamide, the crystalline ordering of the polymers increases, which leads to change in the heats of melting, sorption properties, specific weights, stability towards hydrolytic agents and in the elasticity modulus of the fibres.

An especially sharp change in many properties of the polyamides has been shown to occur on passing from polycapramide to polyenanthamide. This points out to the complexity in the manifestation of the mixed structure of such molecules, requiring account of both the hydrocarbon and carbamide molecular components of the chain.

STUDIES ON THE MOLECULAR STRUCTURE OF SYNTHETIC FIBRES—XV. THERMOCHEMICAL PROPERTIES OF POLYCAPRAMIDE-POLYUNDECANAMIDE POLYMERS OF THE POLYAMIDE SERIES

N. V. Mikhailov and E. Z. Fainberg, Vysokomol. soedin. 1: No. 2, 201–207, 1959.

A COMPARATIVE study has been made of the thermochemical properties of polycapramidepolyundecanamide, polymers of the polyamide series. Based on measurements of the heat capacities and heat effects of solution and on other observations, it has been shown that with increase in the number of methylene groups in the polyamide chain two opposite but correlated phenomena are manifested, namely, increase in molecular chain flexibility and increase in the crystalline ordering of the polymer.

The absence of a linear relation between the heat capacity and molar percentage of the amide bonds has been established over the entire series of polyamides with odd and even numbers of methylene groups. This is a manifestation of the dual character of the polyamides.

It should be expected that on further increase in the number of methylene groups in the polyamide chain (> 10) its properties, the heat capacity in particular, will significantly differ from polyethylene.

EFFECT OF COMPLEXATION ON THE PROPERTIES OF POLYMETHYLMETHACRYLATE SOLUTIONS

A. I. Shatenshtein, and N. A. Pravikova, Vysokomol. soedin. 1: No. 2, 215–221, 1959.

THE formation of molecular compounds in systems composed of the methyl ester of *iso*butyric acid (model of polymethylmethacrylate) and $AsCl_3$ (or $CHCl_3$) has been demonstrated by methods of physico-chemical analysis. The molecular interaction of the polymer itself with the solvent or with added extraneous complexing agents ($FeCl_4$,$TiCl_3$) greatly affects the properties of polymethylmethacrylate solutions.

STUDIES ON THE MOLECULAR STRUCTURE OF POLYAMIDE FIBRES.—XVII. INVESTIGATION OF THE SORPTION PROPERTIES OF POLYAMIDE FIBRES AS A FUNCTION OF THEIR STRUCTURE

Z. G. Serebriakova and N. V. Mikhailov, Vysokomol. soedin. 1: No. 2, 222–229, 1959.

IN a study of the sorption of water vapour by polyamide fibres with respect to their structure it has been shown that the difference between sorption of the vapour by crystalline or by amorphous caprolactam is not one in principle, i.e. that the sorption is not related to the character of the phase structure. The difference is only due to the molecular packing density, which may be changed within sufficiently broad limits under the conditions of forming. By changing the molecular packing density of polyamides in the process of drawing fibres from the melt, equilibrium sorption may be varied over a broad range of values, allowing amorphous and crystalline fibres to be obtained with the same sorption properties. Changes in the physical structure, i.e., in the mutual arrangement of the chains or in the degree of crystallinity of the polyamides brought about in any way, always lead to changes in the sorption properties and open the way for controlling them in the desired direction.

THE DIFFUSION THEORY OF ADHESION

S. S. Voyutskii, Vysokomol. soedin. 1: No. 2, 230–239, 1959.

In the paper a brief discussion has been presented of the various conceptions as to the mutual adhesion of polymers and a theory has been proposed in accordance with which both the adhesion and autohesion of polymers is due to the diffusion of chain molecules, or of their segments, resulting in the formation of a strong bond between the adhesive and substrate. From the standpoint of the proposed theory, the effect on adhesion has been examined and explained for such factors as the duration of contact between the adhesive and substrate, temperature, molecular weight of the adhesive and the shape and polarity of the macromolecules.

ON THE TEMPERATURE DEPENDENCE OF THE DEFORMATION OF CRYSTALLINE POLYMERS

G. L. Slonimskii and V. A. Ershova, Vysokomol. soedin. 1: No. 2, 240–243, 1959.

A study has been made of the mechanical properties of polyhexamethyleneadipamide over a wide range of temperatures. Anomalies have been found in the temperature dependence of the deformability and recrystallization stress in the interval 180–190°C. It has been suggested that the anomalies are associated with the kinetics of crystallization and resrystallization of the polymer.

SOLUBILITY AND THERMOMECHANICAL PROPERTIES OF POLYALUMO-ORGANOSILOXANES

K. A. Andrianov, G. L. Slominskii, T. A. Dikareva and E. Z. Asnovich, Vysokomol. soedin. 1: No. 2, 244–247, 1959.

It has been shown that the addition of plasticizers gives rise to fusibility and fluidity among soluble but non-fusible polyalumo-organosiloxanes, which confirms the absence in them of a three-dimensional structure.

It has been suggested that the non-fusibility of the polyalumo-organosiloxanes investigated is caused by the increased rigidity of their molecules, resulting in a high vitrification temperature and loose molecular packing.

POLYMERIZATION OF N-CARBOXY- AND N-CARBALKOXYPHENYLMETHACRYLAMIDES

G. M. Chetyrkina, T. A. Sokolova and M. M. Koton, Vysokomol. soedin. 1: No. 2, 248–253, 1959.

The process of polymerization in block and in various solvents has been studied of formula $ROOCC_6H_4NHCOC(CH_3)=CH_2$ where R = H, CH_3, C_2H_5 and C_4H_9.

With respect to the polymerization rate in block, the compounds form the series *ortho* > *para* > *meta*.

The rate of polymerization of the carbalkoxyphenylmethacrylamides in dioxane solution is almost the same and is practically independent of the length of the alkyl radical (C_1–C_4).

Polymers of the *para* series possess higher vitrification temperatures than of the isomeric series. At the same time polymers of the *ortho* series have higher intrinsic viscosity values.

The effect of the nature of the solvents (dioxane, chloroform, dimethylformamide, tetrahydrofuran) on the process of polymerization of carbalkoxyphenylmethacrylamides has been shown.

POLYMERIZATION IN SYSTEMS PRODUCED BY THE MOLECULAR RAY METHOD

V. A. Kargin, V. A. Kabanov and V. P. Zubov, Vysokomol. soedin. 1: No. 2, 265–268, 1959.

As illustrated with the aid of beryllium chloride, lithium chloride and metallic magnesium, it has been shown that for the effective initiation of polymerization, crystalline substances may be employed dispersed in the monomer medium to atomic dimensions. In the crystalline state under ordinary conditions, these substances are not initiators of polymerization.

ON THE STRUCTURE OF CELLULOSE—I

A. I. Kitaigorodskii and D. Ia. Tsvankin, Vysokomol. soedin. 1: No. 2, 269–278, 1959.

THE phenomenon of one-dimensional diffraction on cellulose fibres has been studied with a view to the characterization of the degree of ordering in the cellulose structure.

Employing various models, with the aid of the diffraction theory an analysis has been made of the formulas for the intensities of one-dimensional diffraction for the case of parallel chain molecules.

The one-dimensional diffraction on the meridian of non-zero layer lines is discriminated from the reflexes OKO by means of a series of inclined X-radiograms. The presence of one-dimensional diffraction on the meridian and the slow decline in intensity with increasing angle, has been explained in the basis of the theoretical intensity curves with correction for the deviation of the axes of some regions from the texture axis.

A comparison of the intensity distribution on the zero layer line with the theoretical curves for the different models has shown that cause of the one-dimensional diffraction is the statistical deviation of chains from the regular positions corresponding to the tri-dimensional ordering.

ON THE STRUCTURE OF CELLULOSE—II

A. I. Kitaigorodskii and D. Ia. Tsvankin, Vysokomol. soedin. 1: No. 2, 279–286, 1959.

THE X-ray analysis of the degree of ordering in the cellulose structure has been continued [1]. It has been shown that a widening of the lines may be caused by the progressive radial disordering in the equatorial plane: $\Delta p_{mm'} = k p_{m'm}$. Here k = const. and p_{mm} is the distance between the chains m and m' in the undistorted lattice. In this case the width of the lines is independent of the wave length. An estimation of k from the line width gives a value of about 0·05 for the case of viscose.

A comparison of the position of an amorphous halo appearing on the X-radiograms of disintegrated specimens with the theoretical intensity curve, shows that the azimuthal ordering is preserved even in the case of considerable distruction.

Evaluations of the mean squares of the deviation along the axis b $\sqrt{\overline{\Delta n_C^2}} \approx 1$ Å and in the equatorial plane $\sqrt{\overline{\Delta p_C^2}} \approx 0{\cdot}8$ Å were made by measuring the intensities of the one-dimensional diffraction for different layer lines.

A discussion of the results (including data from [1]) has led to the conclusion that in the structure there are no crystalline or amorphous regions separated by boundaries, a typical structural element being a group of chains packed in a 'poor' tri-dimensional order.

ON HETEROCHAIN POLYAMIDES—XII. POLYMER ISOMORPHISM IN THE POLYAMIDE SERIES

T. M. Frunze and V. V. Korshak, Vysokomol. soedin. 1: No. 2, 287–292, 1959.

With the objective of ascertaining as to what structural features facilitate or hinder the appearance of polymer isomorphism and the extent of their action, a study has been made of a number of mixed polyamide systems. It has been shown that the sulphide and sulphonic groups as well as units of *p'*-xylylenediamine and hexamethylenediamine substitute each other quite well, forming isomorphic systems of polyamides.

In the case of systems of mixed polyamides with completely equal chain lengths, but differing in the 'alignment' of the amide groups the phenomenon of polymer isomorphism is not observed.

ON HETEROCHAIN POLYAMIDES—XIII. MIXED POLYAMIDES CONTAINING SULPHUR ATOMS IN THE PRINCIPAL CHAINS

T. M. Frunze and V. V. Korshak, Vysokomol. soedin. 1: No. 2, 293–300, 1959.

Two and three component systems of polyamides have been synthesised in which hexamethylenediamine salts of adipic, azelaic or sebacic acids have been combined in different proportions with ε-caprolactam and hexamethylenediamine salts of thio- or sulphonyldivaleric acids. The mixed polyamides with a specific viscosity in 0·5% tricresol solution of 0·6–0·7 are white, horny products, in some cases translucent. They give fibres capable of cold drawing. The polyamides are insoluble in benzene and acetone, but some are soluble to a certain extent in alcohols, particularly in mixtures of alcohols with chlorinated hydrocarbons. As a rule the most soluble are polymers with the lowest melting temperatures.

The results showed that introduction of sulphide sulphur in the principal chain of the mixed polyamide changes the properties (solubility and melting temperature) more sharply than introduction of sulphonic sulphur. The mixed polyamides are observed to be of diminished thermal stability, which is explained, evidently, by the lower strength of the C–S bond in comparison with the C–C and C–N bond.

ON THE RELATION BETWEEN THE CONFIGURATION OF FIBROUS PROTEINS AND THEIR CHEMICAL STRUCTURE

N. S. Andreeva, Vysokomol. soedin. 1: No. 2, 308–314, 1959.

An analysis has been made of the dependence of the configuration of the more important fibrous proteins on their chemical structure. The known configurations of the polypeptide chains of fibrous proteins are divided into two groups; namely, those insentive to the sequence of the amino acids along the peptide chains and those determined specifically by the arrangement of the amino acid residues.

It has been shown that to the first group, including all α-structures, may be referred proteins with statistical or near statistical arrangement of amino acid residues along the chain. The sharp deviation form the statisticity law—accumulation of a number of groups in some regions of the chains—leads to the appearance of a specific configuration in individual chain fragments. This is characteristic of proteins of the collagen group and silk fibroin.

An X-ray diffraction criterion has been developed for determining the type of configuration of the chain. It has been shown that for the statistical or near statistical arrangement of the amino acids the most ordered structures should be those with one-dimensional periodicity in the chain segment packing. In the presence of accumulations of definite groups in given sections of the chain the formation is possible of regions of short range two- or three-dimensional order.

CERTAIN CORRELATIONS IN THE DEVELOPMENT OF UNIAXIAL DEFORMATION IN CRASTALLINE AND VITREOUS FILMS FROM POLYETHYLENETEREPHTHALATE

P. V. Kozlov, V. A. Kabanov and A. A. Frolova, Vysokomol. soedin. 1: No. 2. 324–329, 1959.

WITH polyethyleneterephthalate for example, a number of general relations have been examined, observed in the uniaxial deformation of films in the vitreous and crystalline states. It has been shown that formation of the so-called 'neck' which may take place during the cold drawing of crystalline and forced elasticity, deformation of amorphous polymers is not due to phase transitions, but is of a relaxation nature.

The results obtained may be interpreted on the basis of the 'packed' structure conception of crystalline and amorphous polymers, developed by Kargin, Kitaigorodskii and Slonimskii.

CHEMICAL GRAFTING ON CRYSTALLINE SURFACES

V. A. Kargin and N. A. Platé, Vysokomol. soedin. 1: No. 2, 330–331, 1959.

THE processes of intensive mechanical disintegration of a number of inorganic crystalline substances have been utilized for initiating the polymerization of several monomers and for the grafting of polymers to these substances.

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* VOL. 1, No. 3, 1959 *

STUDIES ON THE PHYSICO-CHEMICAL PROPERTIES OF CORD FIBRES—II. THE EFFECT OF HEAT AND MECHANICAL TREATMENTS ON THE SORPTION PROPERTIES OF CAPRON CORD

V. A. Berestnev, T. V. Gatovskaia, V. A. Kargin and E. Ia. Iaminskaia, Vysokomol. soedin. 1: No. 3, 337–341, 1959.

ISOTHERMS of the sorption of water and formic acid vapours on capron cord fibres subjected to various treatments, were obtained with the aid of the McBain spiral balance. The effect of the initial heating, plasticization with water, elongation and ultimate breakdown (mastication) of the cord was investigated. Based on the experimental findings it is concluded that the change in sorption properties observed with these treatments are the results of opposite effects: a drop in the sorption capacity due to increase in the molecular packing density during heating and increase in the sorption capacity owing to loosening of the packing on orientation of the chains. On treatment of the capron cord with water, the hygroscopicity of the former also increases owing to increasing flexibility of the molecular chains.

The adsorption isotherms of formic acid for the same objetes practically coincide since this acid is a good solvent of polycaprolactam.

ON HETEROCHAIN POLYAMIDES—XIV. AMORPHOUS STRUCTURES OF POLYAMIDES

T. M. Frunze, V. V. Korshak and V. A. Makarkin, Vysokomol. soedin. 1: No. 3, 342–248, 1959.

THE relation between the structure of mixed linear polyamides and their capacity for forming amorphous structures on quick cooling 'quenching', of a polymer melt at temperatures ranging from −70 to 70° has been investigated. The tendency to form amorphous structures by means of 'quenching' has been found to increase in the mixed polymers with decrease in regularity of structure of the macromolecules. The amorphous structures of the polyamides obtained in this manner are stable only at low temperatures; elevating the temperature leads to gradual crystallization. The presence of water facilitates the crystallization process of the 'quenched' polyamides. With increase in the degree of crystallinity the ultimate forced elasticity increases and ultimate elongation decreases.

ON HETEROCHAIN POLYAMIDES—XV. POLYAMIDES OF HYDROAROMATIC ACIDS

T. M. Frunze, V. V. Korshak and V. F. Petrova, Vysokomol. soedin. 1: No. 3, 349–356, 1959.

POLYAMIDES have been obtained from the salts of hexamethylenediamine and the *cis*- and *trans*-isomers of hexahydrophthalic, hexahydro*iso*phthalic and hexahydroterephthalic

* English abstracts reprinted from Vysokomol. soedin. 1: No. 3, 1959.

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acids. Under the conditions of polycondensation, isomerization of the *cis*- to the *trans*-isomers takes place and in all cases polyamides of the *trans*-isomers of the respective acids are formed. The polyamides are very high melting products with low specific viscosities. The melting temperatures of polyamides from the *trans*-isomers of the hydrogenated phthalic acids vary in the same order as those of their aromatic analogues. Mixed polyamides containing hexamethylenediamine adipate or ε-caprolactam residues besides the residues of *trans*-hexahydroisophthalic acid possess melting temperature minima corresponding to a 30 mol. % content of the hydroaromatic component.

CARBOCHAIN POLYMERS AND COPOLYMERS—XI. THE SYNTHESIS, POLYMERIZATION AND COPOLYMERIZATION OF ESTERS OF VINYLPHOSPHINIC ACID

H.S. Kolesnikov, E.F. Rodionova and L.S. Federova, Vysokomol. soedin. 1: No. 3, 367–372, 1959.

THE synthesis of monomer esters of vinylphosphinic acid has been described and it has been shown that they polymerize on heating in the presence of benzoyl perioxide. The glass temperature of the polymers synthesised was determined. The esters have been found to copolymerize with acrylonitrile, the content of vinylphosphinic ester residues always being lower than in the initial monomer mixture. The copolymer of the ethyl ester has a glass temperature of 90–100° C.

STUDIES ON THE PHYSICO-CHEMICAL PROPERTIES OF CORD FIBRES—III. SOME CHANGES IN THE STRUCTURE OF FIBRES TAKING PLACE DURING REPEATED CYCLIC STRETCHING

V. A. Berestnev, T. V. Gatovskaia, V. A. Kargin and E. Ia. Iaminskaia, Vysokomol. soedin. 1: No. 3, 373–377, 1959.

THE changes in the molecular structure of capron cord fibres taking place on repeated cyclic stretching were investigated by means of thermodynamic methods (determination of the hygroscopicity and the integral heat effects of dissolution in formic acid). The experimental results enabled an assumption to be made as to the possible mechanism of fatigue of the fibres.

DEPENDENCE OF SOLUTION PROPERTIES ON POLYMER STRUCTURE—I. THE VISCOSITY OF SOLUTIONS AND THE MOLECULAR WEIGHT OF A MIXED POLYAMIDE

S. A. Pavlova and S. R. Rafikov, Vysokomol. soedin. 1: No. 3, 387–394, 1959.

THE molecular weights of specimens of a mixed polaymide have been determined from data on light scattering in ethanol solution and by the end group method. The relation between the molecular weight of the polyamide and its viscosity in solutions of cresol, formic acid and ethanol, is expressed by the following formulae: $(\eta)=67{\cdot}5\times10^{-4}M^{0{\cdot}52}$, $(\eta)=1{\cdot}08\times10^{-4}M^{1{\cdot}08}$ and $(\eta)=3{\cdot}39\times10^{-4}M^{0{\cdot}72}$, respectively.

The values for the molecular weights obtained by both methods are in close agreement.

ON THE CONCEPTIONS OF 'SOLVENT' AND 'SOLVENT POWER'

S. P. Papkov, Vysokomol. soedin. 1: No. 395–399, 1959.

THE conceptions of 'solvent' and 'solvent power' are discussed from the standpoint of phase equilibria. The solvent is defined as a liquid which in a given temperature range forms a one-phase thermodynamically stable solution with a given polymer for any quantitative ratios of the components. The arbitrariness of the conception of 'solvent power' has been shown.

ON THE COMPATIBILITY AND MECHANISM OF STABILIZATION OF FIBRE-FORMING POLYMER MIXTURES

N. V. Mikhailov, L. G. Tokareva and E. Z. Fainberg, Vysokomol. soedin. 1: No. 3, 404–409, 1959.

IN the report the results have been presented of a study on the compatibility of the polymers: diacetyl cellulose and chlorinated polyvinylchloride, and nitrocellulose and chlorinated polyvinylchloride. This was based on measurements of the heat effects of dissolution and of the thermo-oxidative breakdown of the polymers mixed in a common solvent and mixed mechanically.

Polymer additions were shown to exert a stabilizing and platicizing effect on the polymers. Based on studies on nitrocellulose and chlorinated polyvinylchloride for example, a reciprocal stabilizing effect was shown of the components of the mixture.

The total thermodynamical and thermo-oxidation data obtained confirm the previously made assumption as to the existence of a stabilizing mechanism caused by intermolecular bond changes, leading to strengthening of the labile group linking in the molecule.

STUDIES IN THE MOLECULAR STRUCTURE OF SYNTHETIC FIBRES—XVI. THE SORPTION OF WATER VAPOURS AND THE HEAT EFFECTS OF WETTING OF ENANTH FIBRES BY WATER

N. V. Mikhailov and E. Z. Fainberg, Vysokomol. soedin. 1: No. 3, 410–414, 1959.

A DETAILED study has been made of the hygroscopic properties of enanth fibres, comprising determination of the water vapour sorption isotherms and the differential and integral heat effects of wetting by water. The results lead to the conclusion that in comparison with polycapramide polyenanthamide possesses an increased tendency to crystallize which is brought out during the cold drawing process. This points out to the possibility of obtaining enanth fibres with improved physico-mechanical properties as compared with fibres from polycapramide.

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COPOLYMERIZATION OF 1,3-BUTADIENE AND 2-METHYL-5-VINYLPYRIDINE

V. L. Tsailingol'd, M. I. Farberov and G. A. Bugrova, Vysokomol. soedin. 1: No. 3, 415–419, 1959.

EXPERIMENTAL data are presented on the copolymerization of butadiene and 2-methyl-5-vinylpyridine. The rate of polymerization has been found to increase with increasing content of the latter compound in the initial mixture.

Calculation of the copolymerization constants on the basis of data on the copolymer composition gave an r_1 value (for 2-methyl-5-vinylpyridine) of $0{\cdot}72 \pm 0{\cdot}03$ and an r_2 value (for butadiene) of $1{\cdot}32 \pm 0{\cdot}01$.

The copolymer composition was calculated and it was shown that the experimental results are in good agreement with the calculated values.

A STUDY OF THE TEMPERATURE DEPENDENCE OF THE TURBIDITY OF CONCENTRATED POLYMETHACRYLIC ACID SOLUTIONS

Yu. S. Lipatov, P. I. Zubov and E. A. Andryushenko, Vysokomol. soedin. 1: No. 3, 425–431, 1959.

THE temperature dependence of the turbidity of polymethacrylic acid solutions in water, 0·01 N HCl, methanol and a mixture of methanol and methylethylketone, as well as in aqueous solutions with the addition of NaCl and of urea has been studied nephelometrically. It

has been found that gel formation on heating is accompanied by a sharp increase in turbidity of the solutions at temperatures depending upon the concentration of the solution and type of addition.

On the basis of the data obtained the heats of aggregation have been calculated and found equal to $-11{,}400$, $-45{,}500$ and $-19{,}700$ in water, 0·01 N HCl and 0·01 N NaCl respectively. No gelation is observed on adding to the aqueous solutions NaOH to the extent of 2% neutralization and on adding urea (5 M). For solutions of polymethacrylic acid in methanol containing a precipitant increase in turbidity is also observed on raising the temperature.

It is suggested that structuration of polymethacrylic acid in aqueous solutions on heating is associated with partial loss of solubility of the polymer and with the aggregation processes taking place between molecules in the coiled globular form.

ON THE GELATION OF CONCENTRATED POLYMETHACRYLIC ACID SOLUTIONS

Yu. Lipatov and P. I. Zubov, Vysokomol. soedin. 1: No. 3, 432–437, 1959.

A STUDY has been made of the specific viscosity of 1–8% solutions of polymethacrylic acid in water 0·01 N HCl, methanol and a mixture of methanol and methyethyl ketone at temperatures of 20, 50 and 60°. With increase in concentration of the polymer in water and HCl, a change in sign is observed of the temperature coefficient of viscosity. Beginning with 6% concentrations the viscosity of solutions at elevated temperatures exceeds that at 20° C and at 8% concentration gelation takes place on heating. On the basis of the findings it has been concluded that gelation of concentrated polymethacrylic acid solutions is associated with partial loss of solubility and is due to aggregation of molecules existing in the coiled state. In the case of methanol solutions and of mixtures of methanol with a precipitant, a decrease in the specific viscosity takes place on heating. It has been found that the viscosity of an 8% polymethacrylic acid solution in water and HCl is higher than the viscosity of an 8% solution of the polyacid neutralized to the extent of 25%.

CHOICE OF A MEMBRANE FOR THE OSMOTIC DETERMINATION OF THE MOLECULAR WEIGHT OF LOW MOLECULAR POLYAMIDES

S. A. Pavlova and I. I. Tverdokhlebova, Vysokomol. soedin. 1: No. 3, 438–442, 1959,

WORK has been carried out on the selection of a membrane for the low molecular nonfractionated mixed polyamide anide H-669. It was found that the size of the pores of a clamped cellophane membrane depends upon the character of the alcohol treatment and on the water content of the alcohol. When membranes twice washed with alcohol were used, molecular weights were found close to values obtained by the end group method ($M_{osm} = 12{,}150$, $M_{end} = 11{,}000$). Membranes treated with alcohol for 24 hr and for a week proved to be very permeable and unsuitable for molecular weight determination of the mixed polyamide. The most suitable membrane for this polymer was found to be moist cellophane 100-130 μ thick twice washed with 75% ethanol.

ON THE POLYMERIZATION OF GLYCIDYL METHACRYLATE

I. A. Arbuzova and V. N. Efremova, Vysokomol. soedin. 1: No. 3, 455–459, 1959.

A STUDY has been made of the polymerization of the glycidyl ester of methacrylic acid in the presence of a radical type of initiator. It was established that polymerization in the bulk proceeds similarly to the polymerization of methylmethacrylate. The presense of an epoxide ring in the side chain of the polymer does not affect the nature of the process and the degree of conversion of the monomer to the polymer. The block polymer is insoluble in the

ordinary organic solvents, has a glass point of 46°, d^{20} 1·2966 and a molar contraction during polymerization of 20·65%. Polymerization in solvents yields a linear polymer. Analysis of the polymer showed that the process takes place at the vinyl bond without participation of the glycidyl group.

POLYMERIZATION OF STYRENE BY THE SIMULTANEOUS ACTION OF CATALYST AND LIGHT

E. V. Zabolotskaia, A. P. Gantmakher and S. S. Medvedev, Vysokomol. soedin. 1: No. 3, 460–465, 1959.

In the polymerization of styrene by the simultaneous action of tin tetrachloride and light, the tetrachloride has been found to be reduced to the dichloride. It has been shown that reduction of the tin is not caused by the presence of radicals in the system 'tin tetrachloride-solvent'. In order for the reaction to proceed in the presence of radicals two of them must collide simultaneously with a molecule of tin tetrachloride. This may be brought about by the interaction of a radical with an ion pair. The formation of bivalent tin is connected with a decrease in concentration of active centres in the system, lowering the over-all polymerization rate and correspondingly causing deviation from additivity.

ON THE METHOD OF MEASURING THE INFRA-RED SPECTRA OF CELLULOSE MATERIALS

I. N. Ermolenko and S. S. Gusev, Vysokomol. soedin. 1: No. 3. 466–472, 1959.

A number of phenomena in the interaction between fibres themselves and between fibres and solids which are observed in the high pressure processing of modified cellulose materials have been investigated with the aid of spectroscopic and radiometric methods. The effects have been studied that may influence the applicability of the previously proposed methods for interpreting the infra-red absorption spectra of fibrous materials.

It has been shown that interaction between fibres during the high pressure treatment of various modified celluloses, depends mainly on the nature rather than on the content of the incorporated functional groups. This is due to the heterogeneous character of the majority of reactions with the participation of cellulose and that packing of the fibres under pressure depends primarily on the properties of their surfaces. In a number of cases interaction between the fibres and alkaline halides used as immersion media and with the introduced internal standard is observed during the compression. Experiments have shown that the method of compressing fibres in the absence of immersion media has a number of advantages when the specimens are intended for spectral measurements. In absolute quantitative determinations it is recommended to estimate the thickness of the specimens radiometrically. For relative measurements of the absorption spectra of fibres of similar composition the thickness may be measured satisfactorily with an optimeter.

INFRA-RED DICHROISM AND THE STRUCTURE OF STEREOSPECIFIC POLYMERS

Iu. Ia. Gotlib, Vysokomol. soedin. 1: No. 3, 474–481, 1959.

It has been shown that the stereochemical structure of a polymer may be determined from a comparison of the dichroic relations. $R = (\varepsilon_\pi - \varepsilon_\sigma)/(\varepsilon_\pi + 2\varepsilon_\sigma)$ for bands corresponding to certain types of vibrations of the CH_2 and CHR groups in *iso* or *syn*dyotactic polymers (-CH_2-CHR-)$_n$. Analysis of the ratios R(j)/R(k) for two bands allows the cancellation of an unknown factor, connected with the orientation of the chains in stretched films. In the case of atactic polymers comparison of the dichroisms in complex bands may in certain cases give evidence as to the degree of stereoregularity of the polymer. Account of the connection between the vibrations

of adjacent groups leads to splitting of the bands, the character of the splitting and the polarization and intensity of the split components also depending upon the stereochemical structure.

ORGANOTIN POLYMERS

D. A. Kochkin, V. N. Kotrelev, M. F. Shostakovskii, S. P. Kalinina, G. I. Kuznetsova and V. V. Borisenko, Vysokomol. soedin. 1: No. 3, 482–484, 1959.

THE possibility has been established of obtaining polymers on the basis of trialkylstannylmethacrylates and dialkylstannyldimethacrylates. The synthesis of such polymers and copolymers has been carried out. A more detailed description is given of polytriethylstannylmethacrylate and its copolymers with various monomers and also some data are presented on the thermomechanical and physico-mechanical properties of these products.

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PAPERS FROM *VYSOKOMOLEKULIARNYE SOEDINENIIA* TO BE PUBLISHED IN FULL IN *POLYMER SCIENCE: U.S.S.R.* VOL. 1, No. 2, 1960

S. R. RAFIKOV and R. A. SOROKINA: Chemical changes of polymers.

M. F. SHOSTAKOVSKII, E. N. PRILEZHAEVA and V. M. KARAVAEVA: Synthesis of sulphur compounds on the basis of vinyl ethers and acetylene.

E. V. FRISMAN, M. A. SIBILEVA and A. V. KRASNOPEROVA: Hydrodynamic and optical properties of polymer solutions in the high concentration range.

K. A. ANDRIANOV and S. E. IAKUSHKINA: Polymerization of mixed aryl (alkyl) cyclotetrasiloxanes.

G. S. KOLESNIKOV, A. P. SUPRUN and T. A. SOBOLEVA: Carbochain polymers and copolymers.

T. M. FRUNZE, V. V. KORSHAK and V. V. KURASHEV: Organophosphorous polymers.

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O. B. PTITSYN: Geometry of linear polymers.

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T. M. BIRSHTEIN and O. B. PTITSYN: Stereospecificity of polymers as a function of the conditions of polymerization.

B. V. PAVLOV and G. V. KOROLEV: The kinetics of induced polymerization.

I. I. BOLDYREVA, B. A. DOLGOPLOSK and V. A. KROL': Reactions of organometallic compounds with heavy metal salts.

K. A. ANDRIANOV and A. K. DABOGOVA: The polymerization of unsaturated organo-silicon compounds.

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CHEMICAL CHANGES OF POLYMERS — III. THERMAL BREAKDOWN OF POLYAMIDES*

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(*Received* 3 *December* 1958)

THE study of the action of heat on polyamides is of great importance both for processes of polyamide resin treatment, and in elucidation of mechanisms of chemical conversion of polyamides during later stages of polymerization. Nevertheless, processes of breakdown and structure formation of polyamides have not been studied sufficiently and the published data are contradictory and do not make it possible to ascertain the molecular mechanism of polyamide conversion at high temperatures [1–3]. Earlier, one of us found [4] that, when heating poly-hexamethylene-adipamide above 180°C, with water in an inert gas atmosphere, in a soldered tube, the molecular weight of polyamide was appreciably reduced by hydrolysis; in addition, the polyamide completely loses its ability to form fibres and films. Similarly, low-molecular polyamide was formed during continuous heating of aqueous solutions of hexamethylenediamine adipate under similar conditions. Consequently, in both cases the reaction equilibria of polymerization and hydrolysis require determination.

$$x\mathrm{HOOC-R-COOH} + x\mathrm{NH_2R_1NH_2} \underset{+\,\mathrm{H_2O}}{\overset{-\,\mathrm{H_2O}}{\rightleftharpoons}} \mathrm{HO[OCRCONHR_1NH]}_x\mathrm{H}$$

When heating polyhexamethylene-adipamide in the absence of water, but in the presence of air, linkage of polyamide chains was observed in the formation of insoluble and infusible products of three-dimensional structure [5].

Korshak and his collaborators [6] showed that, at high temperatures, separation of carboxyl groups of polyamides takes place, as a result of which further growth of the polyamide chain ceases. Staudinger and Schnell [7] found that, when heating polycaproamide in soldered tubes at 250°C in inert gas or air, the molecular weight decreases and, simultaneously, the carboxyl content increases. They also found that the continuous effect of super-heated steam on this polyamide (5 days at 250°C) causes an abrupt decrease of molecular weight and a simultaneous loss of solidity. Loss of mechanical properties of polyamides, when heated in an inert gas atmosphere [8], was observed by a number of authors.

* Vysokomol. soedin. **1**: No. 4, 549–557, 1959.

Achhammer and his collaborators showed that [1] when heating nylon 66 at high temperatures a great variety of liquid and gaseous products are formed, carbon dioxide being the main product in this case. The amount of liberated carbon dioxide exceeded the free carboxyl content in the polyamide by a factor of 10. The authors assume that the principal tendency in the thermal breakdown of polyamides is the homolytic dissociation ot the $>C-N<$ bond with subsequent liberation of carbon dioxide in "accordance with an unexplained mechanism".

Hasselstrom and his fellow workers [2] heated nylon 66 specimens and observed that the amount of liberated carbon dioxide and ammonia were approximately equivalent. They explained this by the presence of salt bonds in the polyamide chain. Recently Straus and Wall [3], studying the kinetics of thermal dissociation of polyamides at 300–400°C, confirmed the formation of large quantities of corbon dioxide. These authors suppose that, even with careful preliminary drying of polyamides, it is not possible to eliminate small residual amounts of water, so that hydrolysis occurs. They do not dispute the possibility of appearance of free radicals in the dissociation of nylon.

We were most interested in the study of chemical conversions of polyamides at temperatures of the order of 300°C, i. e. in conditions which might occur during processing of some polyamide types into fibres or moulded articles. As subjects for study we chose polyamides of homogeneous structure, polycaproamide and polyhexamethylene-adipamide, and also various mixtures of polyamides. On the basis of the work carried out, it is possible to conclude that the character of chemical conversions of polyamides at high temperatures depends to a considerable extent upon their structure and thermal treatment. The basic reactions are decarboxylation and liberation of ammonia. The amount of liberated ammonia and carbon dioxide can considerably exceed the equivalent carboxyl and amino groups, contents of the original polyamide. This is explained by the hydrolysis, due to residual moisture in the polyamide, even when carefully dried. For polyamides, contained in the chain residue of ε-aminocaproic acid, intramolecular reactions are characteristic, which result in separation of links from any site of the polyamide chain and precipitation of caprolactam.

EXPERIMENTAL PART

The following polyamide specimens were subjected to thermal treatment:

(1) Amide-polyamide, obtained from the salt of adipic acid and hexamethylenediamine (technical product). Molecular weight by viscosity 23,500. Neutralization equivalent of amino-radicals—3500. Neutralization equivalent of carboxyl radicals—28,000. The moisture content in an air-dried specimen was 1·11 per cent.

(2) Polycaproamide-polyamide, prepared by polymerization of caprolactam (technical product). Molecular weight by viscosity—18,500. Neutralization

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equivalent of carboxyl radicals—4700. Amino radicals were not present in the original specimen. The moisture content of the air-dried specimen was 1·54 per cent.

(3) Amide 40/60-polyamide, made of hexamethylenediamine adipate and caprolactam in a proportion of 40 : 60. Molecular weight by viscosity—22,500. The neutralization equivalent of amino-radicals was 18,200. Neutralization equivalent of carboxyl radicals was 15,150. The moisture content of the air-dried specimen was 2·79 per cent.

(4) Amide G-669 polyamide, made of hexamethylenediamine adipate, caprolactam and hexamethylenediamine azeleate, taken in proportions of 25 : 50 : 25 (experimental batch). Molecular weight by viscosity—15,900. Neutralization equivalent of carboxyl radicals—6600. In the original specimen there were no amino-radicals. Moisture content of the air-dried specimen was 2·6 per cent.

All specimens were first dried for 60–80 hr in vacuum at a temperature of 60–100°C. In some tests, carried out with amide, the specimen was immersed in absolute methyl alcohol, left overnight and then the methyl alcohol was poured off and the amide dried in vacuum. The polyamides studied were characterized by viscosity of solutions in *m*-cresol, by the amino and carboxyl contents, by the moisture content of air-dry and dried specimens, and thermomechanical diagrams were also constructed. For amide G-669 and capron stability characteristics were determined. The terminal amino-radicals in amide were determined by titration of the polymer solution in *m*-cresol with 0·05 *N* cresolsulphonic acid using cresol red [9]. The terminal carboxyl radicals were determined by back titration of weak solutions of alkali after treatment with the finely dispersed polyamide [10]. The terminal amino- and carboxyl radicals in polycaproamide and amide 40/60 were determined by titration of the polymer solution in benzyl alcohol with 0·02 *N* hydrochloric acid and sodium hydroxide solution in ethyl alcohol of 70%, using bromophenol blue, or phenolphthalein accordingly. In each case the titre of the solutions was determined by *ω*-aminoenanthic acid.

The neutralization equivalent (ε) of amino- or carboxyl radicals in polyamides was calculated by the following formula: $\varepsilon = 1000/N.a$, where N is the normality of acid or base, a is the acid or base consumption of 1 g polyamide. Solution viscosity was determined in *m*-cresol. Molecular weight was calculated by the following formula [11]:

$$\left(\frac{\eta}{c}\right)_{c \to 0} = 0{\cdot}522 \times 10^{-5} M^{1{\cdot}36};$$

in case of amide and amide 40/60—values of the indicated viscosity of 0·5% solutions were taken.

The moisture content of the specimens was determined by the Fischer [12] reagent. The curves of deformation as a function of compression, depending

on temperature, were chosen from measurements by means of an instrument earlier described [13], and the curves of tension as a function of deformation—by means of the Polanyi instrument.

In the first series of experiments, polyamide was heated in sealed ampoules under small residual inert gas pressure. For this, the weighed polyamide portion (10–15 g) in form of a pellet of $1{\cdot}5\times6\times6$ mm size was placed in an ampoule of 60 ml capacity. The ampoule was subsequently emptied and filled with nitrogen or argon 4–5 times and sealed under vacuum. The ampoules were heated in a 6-tube electric furnace equipped with heat regulator and the reaction products analysed. In order to determine the amount of liberated bases, the contents of the ampoule were rinsed in 2–3 stages with 20–25 ml distilled water. An aliquot of the wash water was titrated with 0·2 N hydrochloric acid, or sulphuric acid solution using phenolphthalein and then methyl orange. The carbon dioxide content in the water extract was determined gravimetrically. After heating, the polymer was characterized by the same methods as the original specimens.

In the second series of experiments, polyamide specimens were heated in an inert gas flow in a retort of 50 ml capacity, with a curved outlet. To this retort, receivers were consecutively joined, containing sulphuric acid (0·2 N) and sodium hydroxide (0·5 N). The inert gas was at first cleaned and dried by passage through two columns filled with pyrogallol and two drying columns containing calcium chloride and phosphorus pentoxide on asbestos fibres.

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RESULTS OF EXPERIMENTS AND DISCUSSION

The results of the first series of experiments regarding heating of amide of molecular weight 23,500 (by viscosity) in sealed ampoules at 300°C are shown in Table 1.

TABLE 1. HEATING OF AMIDE IN SEALED AMPOULES

No. of experiment	Duration of heating (hr)	Molecular weight by viscosity	Neutralization equivalent of amino-radicals	Amount of liberated carbon dioxide (mol/equiv.)	Amount of liberated ammonia (mol/equiv.)
28	13	8600	—	0·31	0·99
67	9	10,500	—	0·28	0·78
32	6	7100	4000	4·76	1·48
30	11	9200	—	2·60	0·77
31	11	7000	7000	7·72	2·26

As is apparent from Table 1, in all of the experiments, the molecular weight of amide by viscosity considerably decreases (by a factor of 2–3). At the same time no regular dependence of molecular weight decrease on the duration of

heating is observed. Apparently the differences in the molecular weight decrease depend on the considerable variations in the moisture content of the specimens in question, though all specimens were dried under the same conditions. After heating, carboxyl radicals in amide were not detected analytically and amino content decreased to an insignificant extent.

The amount of liberated carbon dioxide in the last three experiments exceeds the carboxyl content in the initial amide by a factor of 2·5–7·7. The ammonia liberated exceeds the amino content of the original amide by a factor of 2·2.

The liberated carbon dioxide and ammonia, under experimental conditions, form ammonium carbonate and bicarbonate.

The results obtained can be explained by the fact that, in the conditions described, polyamide hydrolysis occurs with residual moisture in the polymer, and liberation of terminal radicals. In this case the velocity of decarboxylation is greater than that of de-amination.

In order to explain the role of the moisture content of polyamide, experiments were carried out with different amounts of polymer in the ampoule. The data for these experiments are shown in Table 2 (heating temperature 270°C).

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TABLE 2. HEATING OF AMIDE IN SEALED AMPOULES

No. of experiment	Duration of heating (hr)	Free ampoule capacity (ml)	Moisture content of free space (g)	Molecular weight by viscosity	Note
33	5	—	—	24,900	The experiment was carried out in inert gas flow
35	10	50	0·040	21,500	
36	10	40	0·032	21,700	
40	6	30	0·021	18,500	

From Table 2 it is apparent that, when heating amide in a closed system, the smaller the free capacity of the ampoule, the greater will be the fall of molecular weight by viscosity. On the contrary, at the same temperature, but in an open system, with continuous moisture-removal by dry inert gas flow, an increase rather than decrease of molecular weight is observed possibly as a result of polymerization (experiment No. 33). If amide is heated in a sealed ampoule at 300°C in the presence of water excess (2 ml water for 3 g polyamide) for 7 hr, a low-molecular weight polyamide forms, which has a melting point of 206–212°C; the neutralization equivalent of carboxyl is 600, amino—800, molecular weight by viscosity is 2500.

When heating amide in atmosphere of dry inert gas at 300°C, no marked decrease of molecular weight by viscosity was observed, which is apparently

also connected with continuous moisture removal from the reaction mixture (see Table 3).

TABLE 3. AMIDE HEATING IN OPEN SYSTEM AT 300°C

No. of experiment	Duration of of heating (hr)	Molecular weight by viscosity	Loss of weight after heating (%)	Neutralization equivalent of amino-radicals	Amount of separated ammonia and amines in (mol/equiv.)
47	5·5	15,000	6·5	2550	3·40
60	7	20,500	4·6	2700	1·45
69	9	19,800	5·1	3100	1·78

The polyamide breakdown under these conditions can be followed by the change in weight of the specimen and ammonia and amine liberation.

When heating polycaproamide in sealed ampoules, a partial decrease occurs in the molecular weight by viscosity because of hydrolysis, and ammonia and carbon dioxide liberation (Table 4).

TABLE 4. POLYCAPROAMIDE HEATING IN SEALED AMPOULES

No. of experiment	Duration of heating (hr)	Molecular weight by viscosity	Neutralization equivalent of amino-radicals	Amount of separated ammonia in mol. for 1 g polymer	Amount of separated carbon dioxide in mol. for 1 g polymer *
53	8	11,100	6200	0·87	1·47
53-a	12	10,500	5600	0·90	2·09

* Carboxyl radicals in polymer after heating not found.

In spite of lengthy heating, depolymerization of polycaproamide under these conditions occurs only to an insignificant extent. This is apparently the result of the monomer ⇄ polymer equilibrium in the closed system.

Entirely different behaviour is observed when heating polycaproamide in an open system, in inert gas (Table 5).

As is apparent from Table 5, when heating polycaproamide under these conditions, continuous depolymerization takes place with separation of caprolactam.

The fall of molecular weight by viscosity is in proportion with the amount of distilled caprolactam. In this case the polymer ⇄ monomer equilibrium always

moves towards monomer formation. In experiment No. 58 (heating at 350°C) liberation of basic products was observed, and, as is apparent from the concentration viscosity relationship, the Haggins constants change, which seems

TABLE 5. RESULTS OF HEATING POLYCAPROAMIDE IN OPEN SYSTEM

No. of experiment	Temperature (°C)	Duration of heating (hr)	Molecular weight by viscosity	Loss in weight (%)	Neutralization equivalent	
					Amino-radicals	Carboxyl radicals
52	270	6	21,500	5·6	Absent	19,600
48	300	6	14,200	13·7	12,800	9550
49	300	8	13,000	16·6	8200	13,200
50	300	12	10,500	19·4	2900	35,009
58	350	4	6500	41·7	1500	Absent

to be connected with partial fission of polyamide chains (Fig. 1). The presence of separate insoluble, but in cresol substantially swollen, inclusions of three-dimensional polyamide, also explains the latter. When heating polycaproamide,

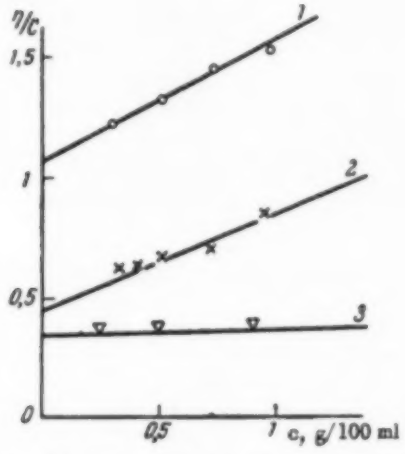
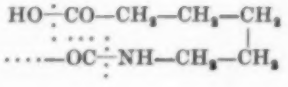
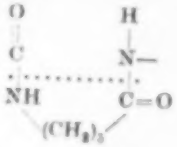


FIG. 1. Dependence of solution viscosity on concentration. (1) Original polycaproamide (2) Polycaproamide heated for 13 hr at 300°C (Experiment No. 50) (3) Polycaproamide heated for 4 hr at 300°C (Experiment No. 58).

depolymerization can occur by intramolecular exchange reactions, taking place at the terminal links of the chain



as also in any section of the chain molecule:



In both cases the decrease of molecular weight will be in proportion to the amount of distilled caprolactam.

The possibility of separation of middle links of the chain, wihout a molecular break, by intra-chain exchange is particularly obvious as confirmed by the experiments carried out in respect of breakdown of mixed polyamides, containing residues of ε-aminocaproic acid in the chain, as, when heating mixed polyamide 40/60 in inert gas flow for 7 hr at 300°C (experiment 45, Table 6)

Table 6. Heating of polyamide 40/60

No. of experiment	Duration of heating (hr)	Molecular weight by viscosity	Neutralization equivalent		Amount of separated ammonia (mol/equiv.)	Amount of separated carbon dioxide (mol/equiv.)
			amino-radicals	carboxyl radicals		
45	7	11,000	4500	30,000	Was not determined *	
33	6	7500	4245	40,000	2·24	0·82
33-a	9	9000	5700	39,450	1·98	0·75

* Distilled caprolactam in a quantity of 13·6% of the weight of polaymide, taken for heating.

Table 7. Heating of amide G-669 in open system

No. of experiment	Duration of heating (hr)	Molecular weight by viscosity	Loss in weight (%)	Neutralization equivalent		Amount of separated ammonia in mol. for 1 g polymer
				Amino-radicals	Carboxyl radicals	
37	4·5	21,400	10·1	11,760	30,100	Was not determined
38	9·5	15,500	21·5	8200	48,500	0·00053
42*	16	10,300	26·1	3200	24,500	0·0007

* Molecular weight of a specimen, which was determined by a light diffusion method, is 13,000.

the loss in weight due to caprolactam distillation was 13·6 per cent. Thus caprolactam separation takes place at the same rate as in the case of homogeneous polycaproamide. When heating in sealed ampoules, no caprolactam precipi-

tation was observed. Only separation of amino- and carboxyl radicals, and partial hydrolysis, took place (experiments 33 and 33a, Table 6).

Similar behaviour was observed when heating mixed polyamide amide G-669 in inert gas flow at 300°C (Table 7). When heating this polyamide in sealed

TABLE 8. HEATING OF AMIDE G-669 IN SEALED AMPOULES

No. of experiment	Temperature (°C)	Duration of heating (hr)	Molecular weight by viscosity	Neutralization equivalent	
				Amino-radicals	Carboxyl radicals
25	300	25	14,200	19,600	11,000
68	300	11	8200	5150	15,500
63	350	7	6700	4100	14,350

ampoules, partial hydrolysis takes place only, with decrease of molecular weight, but without caprolactam separation (Table 8).

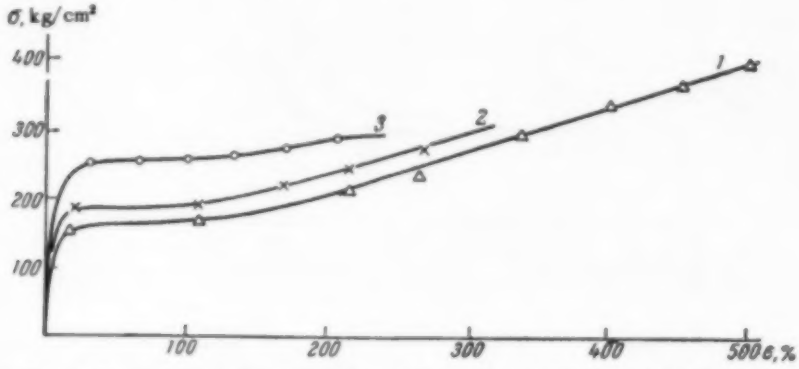


FIG. 2. Dependence of tension (σ) on deformation (ε). (1) Initial amide G-669 (2) Amide G-669, heated for 9·5 hr at 300°C (Experiment No. 38) (3) Amide G-669, heated for 16 hr at 300°C (Experiment No. 42).

In accordance with the separation of caprolactam from the composition of triple mixed polyamide-amide G-669, modification of its mechanical properties and melting point occurs: tensile strength and specific elongation decrease (Fig. 2) and the melting point increases (Fig. 3).

CONCLUSIONS

(1) Study was made of the behaviour of polyamides of different structure at high temperatures.

(2) It was proved that the basic tendencies of chemical conversions of polyamides at high temperatures depend on their structure and on experimental conditions.

(3) In presence of a small amount of moisture, polyamides of the types studied are hydrolysed at comparatively low temperatures. This causes decrease of molecular weight. At 300°C and above, liberation of carboxyl and amino-radicals occurs and hydrolysis is accelerated.

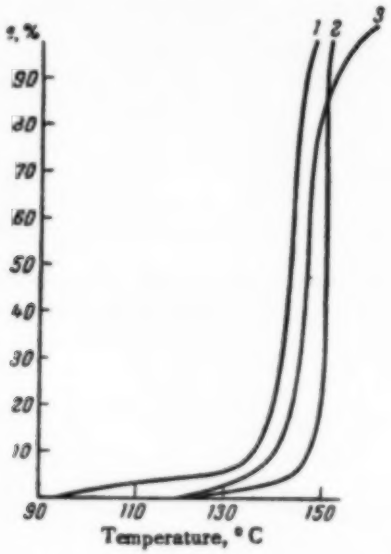


FIG. 3. Dependence of deformation (ε) on temperature. (1) Initial amide G-669 (2) Amide G-669, heated for 9·5 hr at 300°C (Experiment No. 38) (3) Amide G-669, heated for 16 hr at 300°C (Experiment No. 42).

(4) For polycaproamide and its copolymers, the separation of caprolactam from any part of the chain by means of intramolecular exchange is characteristic; in case of continuous removal of the separated monomer, the fall of molecular weight is in proportion to the amount of separated caprolactam.

(5) Molecular weight decrease at the expense of homolytic fission of basic polyamide chains was not observed in any of the polyamide types studied.

Translated by E. SEMERE

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SYNTHESIS OF SULPHUR COMPOUNDS ON THE BASIS OF VINYL ETHERS AND ACETYLENE – XIX. ON THE PART PLAYED BY THIONIC COMPLEXES IN THE IONIC POLYMERIZATION OF SULPHUR-CONTAINING VINYL COMPOUNDS*

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(*Received* 9 *January* 1959)

AS we previously indicated, vinyl sulphides exhibit less activity in ionic polymerization, than the ordinary vinyl ethers, the corresponding oxygen compounds [1, 2]. This was attributed to the smaller nucleophilic activity of the double bond of vinyl sulphides. However quite a number of other data indicate that the nucleophilic activity of the double bond of these compounds is sufficiently high for this purpose. Thus Price and his collaborators, when studying the ultraviolet and infrared spectra of vinyl sulphides, discovered a significant conjugation of the sulphur atom with the double bond [3, 4]. This was fact confirmed by us when studying the combined dispersion spectra of these compounds, where considerable decrease of C=C frequency was revealed with abrupt increase of its intensity in comparison with hydrocarbons. Hence, the conclusion can be drawn that the vinyl sulphide molecule should be easily suffer electron displacement both of the polar type $CH_2{=}CH{-}\ddot{S}R$ and of the double-radical type $\dot{C}H_2{-}CH{-}S\dot{R}$†. Such an effect should promote considerable activity in the reactions both with free radicals and cationic reagents.

The first theory is in fact confirmed—vinyl sulphides polymerize aesily under the influence of a suitable free-radical initiator [1, 5, 6]. In the course of free-radical co-polymerization Price and his collaborators [3, 4] fond high values of the electron stabilization factor Q, which indicate the ease of reaction of C=C-bond with free radicals. The yield of the corresponding copolymers is high [7].

A more careful analysis of the facts concerning vinyl sulphide reactions, confirms that some of these take place at a sufficient speed; e. g. addition of hydrogen halide [8] or dialkyldithiophosphoric acids [9], according to the principle of Mar-

* Vysokomol. soedin. 1: No. 4, 582–589, 1959

† Price [3] assumes the possibility of devolopment of doubleradical condition, which is near the condition developing at light excitation.

kovnikov, to result in a quantitative yield of products and are accompanied by an exothermic effect. At first sight this contradicts the fact that ionic polymerization of vinyl sulphides takes place with great difficulty. However this contradiction can be explained, if it is considered that in a vinyl sulphide molecule there are practically two reaction centres: double bond and hetero-atom with two undivided electron pairs. The ionic addition reactions mentioned above are characterized by the feature that they take place with no catalyst, but the additive reagents, which are strong acids, at the same time will not form complexes with sulphur atoms. Ionic polymerization is a different matter, where metal halides are the catalysts; in this case thionic type complex compounds can, no doubt, develop, particularly having regard to the small concentration of the catalyst and the large excess monomer. (It is known [10, 11], for example that sulphides are good selective adsorbents of BF_3, and the complexes of a number of sulphides with salts of heavy metals serve to identify them). Decrease of the effective concentration of catalyst should result in deceleration of polymerization.

However, the problem of hetero-atom effect on the reactivity of the adjoining double bond is rather complicated. The oxonium theory [12] explains the ease of vinyl ether ionic reactions (with HX reagents) with formation and light dissociation of oxonium complexes with the added reagent or catalyst. In this dissociation, ion formation is possible, which initiates the beginning of the reaction. The ability of oxygen to form unstable complexes, probably eases double bond reactions at the expense of three-dimensional linking of reagents as well. One of us, with Chekulaeva [13], proved that this "activating" effect of oxygen is inhibited, when a nitrogen atom, able to form stable ammonium complexes, is present in the molecule. When studying reactions of vinyl ethers of ethanolamines of $CH_2=CHOCH_2CH_2NR_2$ general formula, it was demonstrated that the greater the basicity of the nitrogen atom (which depends on the nature of the R substitutes), the smaller the tendency to ionic reactions. Gantmakher and Medvedev [14] showed that $AlCl_3$ cannot cause acrylonitrile polymerization, since a stable complex is formed which however, the authors were not able to isolate. It is well-known that the tendency to complex formation of anionic compounds increases with the $O<S<N$ sequence, in which the sulphur atom naturally becomes adjacent to the nitrogen atom, although it forms rather weak complexes.

In order to verify these considerations, a number of sulphur-containing vinyl compounds were synthesized both with and without double bond. The compounds were characterized by the basicity of the sulphur aton. Synthesis of these materials was carried out by means of vinylation of the appropriate mercaptans or alcohols. The polymerization of these compounds under the influence of a number of ionic calalysts: $BF_3.(C_2H_5)_2O$, $SnCl_4$, $FeCl_3.6H_2O$* was studied. The results are shown in Table 1, where the synthesized compounds were arranged in decreasing or-

* We chose this weak ionic catalyst because it is used on an industrial scale for polymerization of ordinary vinyl ethers.

der of tendency to polymerize. From the Table it is apparent, that the ease of polymerization under the effect of one or another catalyst does not actually depend on the properties of the double bond of the given compound, but is rather determined by the basicity of sulphur atom. Thus, vinylphenyl sulphide has the greastet activ-

TABLE 1. IONIC POLYMERIZATION OF SULPHUR-CONTAINING VINYL COMPOUNDS

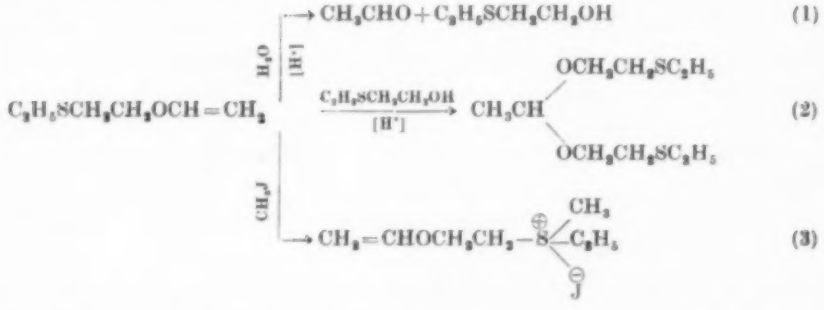
Formula	Reaction conditions: Catalyst: Name	Catalyst: Quantity (%)	Temperature (°C)	Time (hr)	Polymer: Yield (%)	Polymer: Molecular weight	Reference to the literature
$CH_2=CH-\ddot{S}-C_6H_5$	$FeCl_3 \cdot 6H_2O$	1	45	3	68		
	$SnCl_4$	1	45	3	66		
	$BF_3 \cdot (C_2H_5)_2O$	1	35	2	60	3050	—
$CH_2=CHOCH_2CH_2-\ddot{S}-CH=CH_2$	$FeCl_3 \cdot 6H_2O$	1	60	4	45	Liquid	
	$BF_3 \cdot (C_2H_5)_2O$	2 drops			Vigorous resinification		
$CH_2=CH-\ddot{S}-C(CH_3)_3$	$FeCl_3 \cdot 6H_2O$	1	60	3	40	300	
	$BF_3 \cdot (C_2H_5)_2O$	0·5			Vigorous resinification		—
$CH_2=CH-\ddot{S}-C_2H$	$FeCl_3 \cdot 6H_2O$	1	60	3	0	—	
	$SnCl_4$	1	70	2	70		[2]
	$BF_3 \cdot (C_2H_5)_2O$	1	60	3	95	2100	
$CH_2=CH\ddot{S}CH_2CH_2OC_4H_9$	$BF_3 \cdot (C_2H_5)_2O$	1	60	3	62	2800	[2]
$CH_2=CHOCH_2CH_2\ddot{S}C_2H_5$	$FeCl_3 \cdot 6H_2O$	1	90	1	0	—	
	$FeCl_3 \cdot 6H_2O$	1	35/4 mm 65	1	0	—	
	$BF_3 \cdot (C_2H_5)_2O$	5		63	50	2300-2700	
$CH_2=CH-\ddot{S}CH_2$ $CH_2\ddot{S}C_2H_5$	$BF_3 \cdot (C_2H_5)_2O$	1	60	3	—	—	
	$BF_3(C_2H_5)_2O$	30	60	75	10	—	

ity in ionic polymerization and yields polymer in the presence of ferric chloride, apparently because the sulphur atom in its molecule has the lowest complex-forming tendency in view of the fact its free electrons link with the π-electrons of the phenyl group. This type of reaction for various aryl sulphides was demonstrated during the study of their spectra [15]; this is indicated by a considerable increase of

molecular refraction [16], and also by some indirect chemical data [17]. The divinyl ether of monothioethylene glycol polymerizes in the presence of ferric chloride, apparently only in case of the O-vinyl radical, since liquid and not solid three-dimensional polymer develops. However, the minimum amount of catalyst $FeCl_3 \cdot 6H_2O$ (1%) required for this sulphur-containing vinyl compound is considerably higher than for ordinary vinylalkyl ethers (0·01–0·05%) [18]. The strong tendency of tert-butylvinylsulphide to ionic polymerization was rather unexpected; however the polymer obtained had very low molecular weight. It is possible that, in this case an unstable complex develops with the catalyst. There are some indications which point to the instability of mercuric chloride complexes with sulphides, containing the tert-butyl radical on the sulphur atom [19].

None of the vinyl compounds shown in the Table yield polymers in the presence of ferric chloride. β-ethylmercaptoethylvinyl sulphide, containing two sulphur atoms in the molecule, does not polymerize even under the effect of boron trifluoride ester.

It is interesting that 1-mercaptoethyl-2-vinyloxyethane, which definitely does not yield polymers in the presence of ferric chloride (when catalyzed with hydrogen chloride, behaves like typical vinyl ether [12]). Thus it is completely hydrolyzed in 2 hr by N.hydroxylamine hydrochloride solution and quantitatively combines with alcohol with formation of acetals: at the same time it reacts with methyl iodide, forming the iodomethylate as follows:



$$C_2H_5SCH_2CH_2OCH=CH_2 \xrightarrow[[H^+]]{H_2O} CH_3CHO + C_2H_5SCH_2CH_2OH \quad (1)$$

$$C_2H_5SCH_2CH_2OCH=CH_2 \xrightarrow[[H^+]]{C_2H_5SCH_2CH_2OH} CH_3CH(OCH_2CH_2SC_2H_5)_2 \quad (2)$$

$$C_2H_5SCH_2CH_2OCH=CH_2 \xrightarrow{CH_3J} CH_2=CHOCH_2CH_2-\overset{\oplus}{S}(CH_3)(C_2H_5)\ \overset{\ominus}{J} \quad (3)$$

If taking into account that the sulphur atom does not form complexes with hydrogen halides, such behaviour becomes quite understandable. In order to confirm the aforementioned assumptions, an attempt was made to prepare complex compounds of some sulphur-containing and thiovinyl ethers. It was previously shown that vinylethyl sulphide in ether medium yields, with $HgCl_2$, a complex of multiple composition [1]. We did not succeed in separating iodomethylate of vinylethyl sulphide. Nevertheless this should be expected on the basis of well-known work, which has proved the instability of the trialkylvinylsulphonium ion [20].

Interesting results were obtained in the course of reaction of vinylethyl sulphide with anhydrous ferric chloride. This salt slowly dissolves in vinyl sulphide without warming up. After the evaporation of excess vinyl sulphide, viscous, dark-coloured

polymeric residues remain, from which ferric chloride cannot be extracted either with water, or with other solvents. These data indicate the fact that catalyst complexes with sulphides actually develop and, apparently under certain conditions, they themselves act as weak catalysts of polymerization.

The consideration of the data here discussed and the experiments prove the fact that, in the case of ionic polymerization, catalyzed with halides of metals, owing to the presence of a reactive sulphur atom, the process can take an other direction, and the double bond is not affected. The selective reactivity of vinyl sulphides, directed mainly by the sulphur atom, and not by the double bond, can also operate in other reactions of these compounds, as for example in oxidation reactions to vinyl sulphoxides and sulphones [21] or in reaction of vinyl sulphides with mercuric chloride in alcohol medium, leading to a quantitative break of the mercapto-radical [22].

EXPERIMENTAL PART

Synthesis of sulphur-containing vinyl compounds and their reaction are described in the order of these compounds shown in Table 1. Polymerization was carried out in 3-necked small flasks, equipped with stirrer, reflux condenser, thermometer and gas-feed pipe, through which continuously weak, purified, dry nitrogen was passed. For polymerization 5–10 g vinyl compound was taken. The catalyst was added in one dose with the help of a graduated dropping tube through a special opening in the gas-feed pipe. The methods of purifying the polymer are described separately in each case. All molecular weights were determined cryoscopically in benzene. The catalysts of $SnCl_4$ and $BF_3.(C_2H_5)_2O$ were applied freshly distilled and without diluent; $FeCl_3.6H_2O$—in form of 5% solution in dry butanol.

Vinylphenyl sulphide was obtained by vinylizing thiophenol in butanol or dioxane, as previously described [23], and purified by distillation in vacuum on an all-glass column of 20–25 theoretical plates. A fraction with a boiling point of 56°/4 mm, n_D^{20} 1·5890 was used. The distilled vinylphenyl sulphide was kept in sealed ampoules under nitrogen. Distillation was carried out before each experiment, since during storage, vinylphenyl sulphide partially polymerizes. The product purified by this method did not darken during storing, in contrast to the product used previously by Price and his collaborators [4]. Polymerization of vinylphenyl sulphide in the presence of $BF_3.(C_2H_5)_2O$ was carried out at a temperature of 35°C, because at higher temperatures, which are optimum for vinylphenyl sulphides [2], brisk effervescence and carbonization of the reaction mass occurred. Polymers were purified by repeated solution in benzene and precipitation by a tenfold proportion of methanol with subsequent drying in vacuum to constant weight at 60°C.

Divinyl ether monothioethylene glycol (1-vinyloxy-2-vinylmercaptoethane) was obtained by vinylation of the monovinyl ether of ethylene glicol, as described previously [24], and had constants corresponding exactly to the constants given in the literature; boiling point 40°/7mm, n_D^{20}1·4992. It was not possible to obtain

polymer in the presence of $BF_3.(C_2H_5)_2O$, because rapid evaporation occurred and insoluble, dark flakes developed. In the presence of $FeCl_3.6H_2O$, a viscous polymer was obtained, soluble in benzene and dioxane.

Tert-Butylvinyl sulphide. The initial *tert*-butylmercaptan was prepared from *tert*-butyl bromide (obtained from isobutylene and HBr) by reaction with thiocarbamide in alcoholic solution and had a boiling point of 64°/758 mm, n_D^{20}1·4225, which corresponded to data given in literature [16]. *Tert*-butylvinyl sulphide was obtained by vinylation of *tert*-butylmercaptan under conditions indicated in Table 2. The use of dioxane makes vinylation easier, but in wiew of the closeness of the boiling points of *tert*-butylvinyl sulphide and dioxane, and also, the significant solubility of *tert*-butylvinyl sulphide in water (which makes it impossible to remove dioxane by washing) a purer product was obtained in the experiments without any solvent.

TABLE 2. VINYLATION OF *TERT*-BUTYLMERCAPTAN

Taken				Reaction conditions		Yield of thioether (%)
Mercaptan (g)	Acetylene (g)	KOH Molecules (%)	Solvent (ml)	Temperature (°C)	Time (hr)	
12·4	10·0	26	20 ml dioxane	110–130	2	70
16·0	8·5	20	without solvent	140	2·5	50
12·0	9·0	20	—	160	2·5	30

After removal from the autoclave, the reaction mixture vas diluted with sulphuric ether, dried with Na_2SO_4 and distilled. Raw thio-ether had a boiling point of 114–117 °C, $n_D^0$1·4589. After repeated distillations *tert*-butylvinyl sulphide of following properties was obtained: b.p. 112°/744 mm, n_D^{20}1·4622, d_4^{20} 0·8397 (in the literature [25] a boiling point of 117°C, n_D^{20} 1·4622, d^{20} 0·840 was indicated), MR_{found}37·99, $MR_{calc.}$37·47.

Found %: C 61·84; 61·95; H 10·12; 10·45; S 27·23; 27·18
$C_6H_{12}S$. Calculated %: C 62·00; H 10·41; S 27·59

When hydrolyzing by hydroxylamine method (40°C, for 2 hr, 0·1N.NH_2 OH. HCl) 91·5% thio ether content was determined. Titration of *tert*-butylvinyl sulphide by mercuric chloride method [22] proved to be inapplicable, since instead of the expected development of the mercurochloride of *tert*-butylthiol during reaction with mercuric chloride, metallic mercury precipitation was observed; as a result, during 3 hr at 25°C with titration, 1·2 acid equivalent was found. Polymer obtained by the effect of $FeCl_3.6H_2O$ was separated by extracting monomer in vacuum of $2 \cdot 10^{-2}$mm, since in view of low molecular weight it was not possible to purify it by re-precipitation.

Vinylethyl sulphide. Separation [1] and polymerization in the presence of $BF_3.(C_2H_5)_2O$ were previously described in detail [2]. Polymer with $SnCl_4$ was obtained under standard conditions and was purified by re-precipitation from benzene solution with methanol, with subsequent drying in vacuum.

β-Butoxyethylvinyl sulphide. Preparation [22] and polymerization in presence of $BF_3.(C_2H_5)_2O$ were earlier described in detail [2].

1-Mercaptoethyl-2-vinyloxyethane.

(a) *For synthesis*, the vinylation reaction of β-ethylmercaptoethanol (β-EME) was used at 135–145°C in the presence of 20 mol% KOH; the yield was 40–60 per cent. The reaction mass after discharging from the autoclave, and dilution with sulphuric ether, was repeatedly rinsed with water in order to eliminate impurities and unreacted alcohol, and was dried over Na_2SO_4. After evaporation of sulphuric ether and distillation in vacum, 1-mercaptoethyl-2-vinyloxyethane had constants of b.p. 39°/4 mm, n_D^{20}1·4735. After distillation in vacuum on a column of 10–15 theoretical plates, the constants were: b.p. 47·2°/6 mm, n_D^{20} 1·4735, d_4^{20}0·9531, MR_{found}38·91, $MR_{calc.}$39·05.

Found %: C 54·52; 54·58; H 9·03; 9·16; S 24·39; 24·25
$C_6H_{12}OS$. Calculated %: C 54·54 H 9·08; S 24·27

(b) *Hydrolysis by hydroxylamine method* (Equation 1). 0·1982 g 1-mercaptoethyl-2-vinyloxyethane and 10 ml. N. $NH_2OH.HCl$ solution was left for 2 hr at 30–35°C. By titration of 0·1 N. NaOH in the presence of bromophenol blue, the vinyl ether content was found to be 96·7 per cent.

(c) *Addition of β-EME* (Equation 2). To a mixture of 6·6 g (0·05 mole) 1-mercapto-2-vinyloxyethane and 5·3 g (0·05 mole) β-EME in a small flask, with mixer, one drop of 33% hydrochloric acid was added. The temperature was raised to 90°C. The reaction bulk was mixed for 6 hr at room temperature, after which in the course of distillation 11·5 g (90 per cent of the theoretical yield) ββ-dimercaptoethyldiethyl acetal was obtained with a boiling point of 120–122°/3 mm, and n_D^{20}1·4880. After repeated distillation the product had a boiling point of 135°/3·5 mm, and n_D^{20}1·4881, d_4^{20}1·1019, MR_{found}67·44, $MR_{calc.}$67·60 and represented a liquid with a sharp odour, turning slightly violet in colour.

Found %: C 50·43; 50·33; H 9·46; 9·41; S 27·04; 26·99
$C_{10}H_{22}O_2S_2$. Calculated %: C 50·37; H 9·30; S 26·88

(d) *Preparation of iodomethylate* (Equation 3). 6·6 g 1-mercaptoethyl-2-vinyloxyethane (0·05 mole) and 14 g CH_3I (0·1 mole) were mixed in a separating funnel. Next day a heavy, viscous product was deposited. Iodomethylate yield, after washing off with sulphuric ether, and drying in vacuum, was 10·7 g (40 per cent of the theoretical yield). Iodomethylate is difficult to dissolve in dioxane, and is insoluble in other ordinary organic solvents.

Found %: C 29·57; 29·45; H 5·68; 5·64; S+I 11·7+46·24
$C_6H_{12}OS.CH_3I$. Calculated %: C 30·67; H 5·52; S 11·7; I 46·30

(e) *Polymerization*. The effect of $FeCl_3.6H_2O$ was studied not only under standard conditions (90°C, 1 hr), but also by boiling in vacuum. For this, a small flask with dephlegmator, equipped with capillary, was used. 3 g 1-mercaptoethyl-2-vinyloxyethane were added and heated to boiling at a residual pressure of 3 mm

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(36°C) in the presence of 0·03 g $FeCl_3.6H_2O$, in butanol solution. Under these conditions no polymer was obtained. Polymer obtained in the presence of $BF_3.(C_2H_5)_2O$, was purified as usual by precipitation with methanol (in the presence of NH_3) from the solution in benzene. Polymer was dried in vacuum to constant weight.

1-Mercaptoethyl-2-mercaptovinylethane. Initial β-mercaptoethylmercaptan was obtained, as earlier described [1], by the effect of H_2S on vinylethyl sulphide. For vinylation, 7 g product was heated with excess acetylene in a rotating autoclave with 1·4 g KOH in 20 ml. dioxane (110–120°C) for 2 hr. After dilution of the reaction mass with ether, drying above Na_2SO_4 and distillation, the following fractions were obtained:

I fr. 62– 64°/2 mm, n_D^{20} 1·5369–5·1 g
II fr. 150–170°/2 mm, n_D^{20} 1·5711–0·5 g

Fraction I after repeated distillation had a boiling point of 64°/2 mm, with n_D^{20}1·5369, d_4^{20}1·0142, MR_{found}45·65, $MR_{calc.}$45·38 (70 per cent yield of the theoretical value).

$C_6H_{12}S_2$. Found %: C 48·57; 48·54; H 8·28; 8·21; S 43·13; 43·11
Calculated %: C 48·62; H 8·18; S 43·21

When heating 1-mercaptoethyl-2-mercaptovinylethane for 75 hr, (with breaks) in the presence of 30 per cent $BF_3.(C_2H_5)_2O$, a polymer with a yield of 10 per cent was obtained. It gave satisfactory analytical data, but the quantity was insufficient for determination of molecular weight.

Found %: C 48·80; 48·85; H 8·18; 8·18; S 43·50; 43·41

CONCLUSIONS

(1) Study was made of polymerization of a number of sulphur-containing viny compounds under the effect of ionic catalysts such as $BF_3.(C_2H_5)_2$, $SnCl_4$, $FeCl_3.6H_2O$. It was proved that the tendency of these compounds to polymerization is in inverse relation to the basicity of the sulphur atom in the molecule. This fact is explained by devolopment of thionic complex salts with catalyst.

(2) New vinyl compounds were obtained, containing sulphur in the molecule: 1-mercaptoethyl-2-oxyvinylethane, 1-mercaptoethyl-2-mercaptovinylethane.

(3) It was proved that in a similar manner to the reaction of vinylethyl sulphide with $FeCl_3$ sulphur-containing vinyl compounds are able to form complexes with metal halides.

Translated by E. SEMERE

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HYDRODYNAMIC AND OPTICAL PROPERTIES OF POLYMER SOLUTIONS IN THE HIGH CONCENTRATION RANGE*

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(*Received* 17 *November* 1959)

PREFACE

THE study of birefringence during flow of diluted polymer solutions made it possible to draw a number of important conclusions about the properties of the isolated macromolecule [1–10].

The difference of the main polarizabilities of macromolecule $(\gamma_1-\gamma_2)$ (determining birefringence in flow) represents the sum of two terms, one of which is due to natural anisotropy [11], the second to the asymmetry of the form of the spheroid.

$$\gamma_1-\gamma_2=\frac{3}{5}(\alpha_1-\alpha_2)\frac{h^2}{\bar{h}^2}+\left(\frac{n_k^2-n_s^2}{4\pi\rho n_s N_A}\right)^2\frac{M^2}{v}(L_2-L_1)\left(\frac{3}{n_s^2+2}\right)^2=$$

$$=\theta_i\frac{h^2}{\bar{h}^2}+0{\cdot}439\,(L_2-L_1)\,\theta_f=(\gamma_1-\gamma_2)_i+(\gamma_1-\gamma_2)_f\,. \qquad (1)$$

Here $(\alpha_1-\alpha_2)$, is the optical anisotropy of the statistical segment of the chain; h, the distance between the ends of the chain; $\bar{h}^2$, the mean square of the same length for the undistorted macromolecule; n_k and n_s, refractive indices of polymer and solvent, accordingly; M, molecular weight of the polymer; ρ, its density; (L_2-L_1), ratio function of axes of molecular ellipsoid; v, its volume; N_A, Avogadro number.

During acceleration, the macromolecule deforms, altering the values $(\gamma_1-\gamma_2)$. Both terms in the expression for $(\gamma_1-\gamma_2)$ depend in a different way on the deformation of the macromolecular spheroid: the value $(\gamma_1-\gamma_2)_i$, dependent on natural anisotropy, increases more rapidly than the $(\gamma_1-\gamma_2)_f$ value, dependent on the asymmetry of the macromolecular shape.

This causes a dependence of the dynamic birefringence parameter on acceleration for some systems containing macromolecules with negative natural anisotropy [5].

The hydrodynamic force, which deforms the macromolecule in laminar flow, however, depends not only on acceleration (g), but also on the viscosity of the

* Vysokomol. soedin. 1: No. 4, 597–606, 1959.

solution. Therefore the increase of solution concentration (i. e. increase of its viscosity) at a given g in a certain sense is equivalent to the acceleration increase at a given c solution concentration. In fact experience shows that for the systems considered in the range of $g \to 0$, relation of the birefringence parameter with solution concentration is observed [6–10].

One of the reasons, consequently, determining the effect of solution concentration on the Δn value of birefringence, is the displacement stress, deforming the macromolecule with increase of solution concentration. This reason is clearly hydrodynamic. However, the observed decrease of the effect of shape in concentrated solutions is due to another cause, which is clearly of an optical character.

With increase of solution concentration optical heterogeneity diminishes. This is due to the fact that by lessening the distance between the dissolved molecules, the effect of asymmetry of macromolecule shape on their polarizability decreases. Actually, in this case, the optical polarizability of the section depends not only on the field anisotropy formed by other sections of the same molecule, but is also subjected to the influence of sections of other macromolecules, which on an average are evenly distributed in the volume of solvent and level the field asymmetry of sections of the molecule in question [9].

Thus, increase of solution concentration (at a given g) leads to increase of birefringence, caused by natural anisotropy of molecules (hydrodynamic factor), and decrease of birefringence coupled with shape asymmetry of the macromolecular ellipsoid (optical factor).

It is interesting to examine the concentration dependence of these two factors. In this work [9] such a study for a range of limited concentrations was accomplished.

It is well-known that at accelerations and concentrations, approaching zero, birefringence is characterized by a dynamo-optical constant:

$$[n] = \lim_{\substack{g \to 0 \\ c \to 0}} \left(\frac{\Delta n}{gc\eta_0} \right), \tag{2}$$

where $(\Delta n/g)_{g \to 0}$ is the initial slope of the function curve of Δn birefringence value of acceleration for the solution of c concentration; η_0 is the viscosity of solvent.

At the same time $[n]/[\eta]$ ($[\eta]$ is intrinsic viscosity) is related to the total anisotropy of the macromolecule the following way [9,12]:

$$\frac{[n]}{[\eta]} \times \frac{3n_s kT}{4\pi} \left(\frac{3}{n_s^2 + 2} \right)^2 = \theta_i + \theta_f. \tag{3}$$

Here k is the Boltzmann constant; T, absolute temperature; the remaining letters retain the previous meanings.

It was experimentally determined that, when increasing the concentration of solution, containing elastic linear macromolecules and which exhibits no

shape effect, its birefringence $(\Delta n/g)_{g\to 0}$ increases in proportion to $\sqrt{\eta_r}$, where η_r is the relative solution viscosity [1,2,9]. This makes it possible to determine the dynamo-optical constant from the data given for limiting concentrations:

$$[n]=\frac{1}{\sqrt{\eta_r}}\lim_{g\to 0}\left(\frac{\Delta n}{gc\,\eta_0}\right)=\frac{[n]^*}{\sqrt{\eta_r}}\,; \tag{4}$$

$[n]^*$ is the dynamo-optical constant at c concentration. For similar systems $\theta_f=0$ and the equation (3) is rewritten as follows:

$$\frac{[n]^*}{[\eta]\sqrt{\eta_r}}\times\frac{3n_s kT}{4\pi}\left(\frac{3}{n_s^2+2}\right)^2=\theta_i\,. \tag{5}$$

The θ_i values, calculated according to equation (5) remain constant for the concentration range studied up to this point [9]. Thus it seems to be possible to calculate the concentration dependence of the hydrodynamic interaction of macromolecules in the solution.

In solutions, having shape effect, the $[n]^*/\sqrt{\eta_r}$ ratio does not remain constant, but is determined by dependence of θ_f on the solution concentration. In this case the equation (3) can be rewritten as follows:

$$\frac{[n]^*}{[\eta]\sqrt{\eta_r}}\times\frac{3n_s kT}{4\pi}\left(\frac{3}{n_s^2+2}\right)^2=\theta_i+\theta_f^*\,, \tag{6}$$

where θ_f^* is the shape anisotropy in case of the limiting value of solution concentration.

So, if θ_i value is well-known, depending on the solution concentration, it is possible to determine experimentally dependence of θ_f^* on c (Equation 6).

θ_f value can be determined from the Equation [3] by the measured $[n]$ and $[\eta]$ or by extrapolation of $\theta_f^*=f(c)$ curve to $c=0$. The study carried out in this work [9] can be reduced to the dependence of θ_f^* on c as follows:

$$\theta_f^*=\theta_f(1-k_1[\eta]c+k_2[\eta]^2c^2-\ldots)\,. \tag{7}$$

Here k_1 and k_2 > are coefficients.

Hence, the relative initial slopes of $\theta_f^*/\theta_f=f(c)$ dependence curves should be in proportion to the $[\eta]$ characteristic viscosities:

$$-\frac{1}{\theta_f}\left(\frac{d\theta_f^*}{dc}\right)_{c\to 0}=k_1[\eta]\,. \tag{8}$$

Comparison of Equation [8] with experiment gave good results. This confirms the correctness of Equation [7] for extremely small solution concentration ranges.

The object of the present work is to study the hydrodynamic and optical interaction of macromolecules in concentrated solutions. It was interesting

to find out, whether or not the θ_i value, determined by Equation [5], remains constant in the high solution concentration range. If θ_i is correctly calculated, it is possible to find experimentally the character of θ_f^* concentration function and the extent of the shape effect at great c values.

1. SPECIMENS AND METHODS OF STUDY

Four polystyrene fractions, obtained by fractional precipitation, were studied. In fractionation benzene was used as solvent, and methyl alcohol as precipitant.

Molecular weights of fractions are indicated in the Table.

TABLE 1

Fraction	$M10^{-4}$	$[\eta]$ 100 cm³/g (in distance)	$[\eta]$ 100 cm³/g (in bromoform)
I^a	2·50	3·85	3·90
I^b	1·68	2·77	3·10
I	0·70	1·58	1·76
VI	0·20	0·70	0·82

I^a and I^b fractions were obtained by fractionation of specimen of $M \approx 7 \cdot 10^5$, mean molecular weight, and I and VI fractions were obtained from specimens with $M \approx 3 \cdot 10^5$.

Dynamic birefringence of solutions of the indicated fractions were studied in two solvents.

Bromoform was one of the solvents, which satisfies the $n_k = n_s$ condition. Thus, in these solutions no shape effect is present. Dioxane was the second solvent, for which $n_k - n_s = 0{\cdot}18$.

The great difference between the refractive indices of polystyrene and dioxane results in a larger shape effect in these solvents.

In order to measure the value of birefringence in the flow, a dynamo-optical indicator was used with an internal rotor and $l = 3$ cm working length. Since the object of the present work was the study of wide range of concentrations, the limited thickness of the layer studied played a positive role: the volume of the solution studied was limited. Considerable viscosity of the studied solutions excluded the possibility of turbulence development.

For concentrated solutions a rotor was used, which allows a tolerance of $\Delta r_1 = 0{\cdot}10$ cm. Solutions of small concentrations were studied with a tolerance of $\Delta r_2 = 0{\cdot}03$ cm.

Temperature stabilization was effected by a thermostat, type TS-15. The thermostatic liquid was passed through the jacket covering the working layer of the solution.

The optical equipment used with semi-shaded reading was earlier described [2, 13].

In view of the fact that the interval of the measured values of birefringence was very great, we used two compensators with a movement difference of

$$\Delta_1 = 0{\cdot}019\lambda \text{ and } \Delta_2 = 0{\cdot}15\lambda \ (\lambda = 5461 \text{ Å}).$$

The movement difference of compensators was measured by means of a Senarmon compensator. The verification of Δ_1 and Δ_2 values was accomplished by the study of birefringence of standard liquid. By this the correlation of tolerances was checked for the two rotors.

The characteristic fraction viscosities, measured in bromoform and dioxane, are indicated above in the table. Measurements were also made of the relative viscosities at all concentrations, the dynamic birefringence of which was studied. The viscosity and birefringence measurements in the flow were carried out at the same temperature.

2. EXPERIMENTAL DATA

As already indicated, a study was made of the dynamic birefringence of our polystyrene fractions in dioxane and bromoform.

I and VI fraction solutions in dioxane possess negative birefringence over the complete range of concentration and acceleration studied. As to fractions I^a and I^b, their solutions of small concentration in dioxane possess positive birefringence in the small acceleration range, which changes into negative birefringence with the increase of acceleration [5, 6, 10]. Solutions of mean and great concentrations develop negative birefringence at all accelerations.

On Fig. 1. *a*, *b*, *c*, *d*, a graphic representation is given of the dependence of Δn birefringence value on g acceleration for solution of two polystyrene fractions in dioxane. (Since the concentration range studied is very great, the data for each fraction are brought forward in two figures.)

Since the polystyrene solutions in bromoform do not exhibit any shape effect, their birefringence is negative, regardless of the molecular weight of polymer, solution concentration and acceleration.

As an example, the $\Delta n = f(g)$ function is brought forward for solutions of I polystyrene fraction in bromoform (Fig. 1.*e*).

The experimental data show that the dynamo-optical constant $[n]$ is negative only for fraction VI. Although all solutions of I fraction give negative birefringence, $[n]$ for this fraction has very small positive value.

This is explained by the fact that positive birefringence in this case should be observed in a solution of very small concentration, where birefringence is practically immeasurably small. In diluted solutions of I^a and I^b fractions, positive birefringence can be measured at small acceleration.

3. DISCUSSION OF RESULTS

In order to determine θ_f^*, shape anisotropy in wide concentration range, using Equation [6], it is necessary to know the θ_i value. If θ_i is constant, dependence of $(\theta_i + \theta_f)$ on the concentration will be determined only by θ_f^* variation.

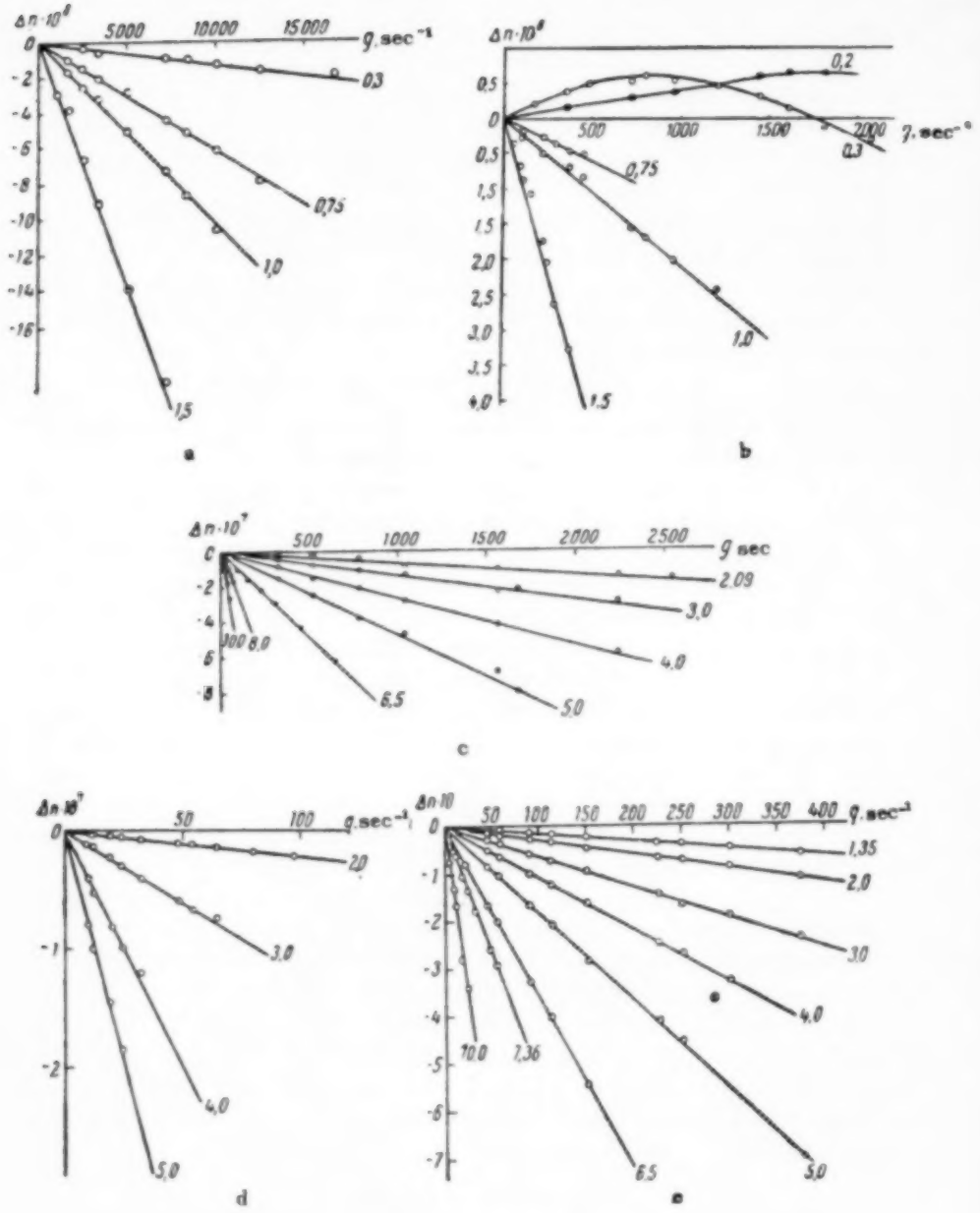
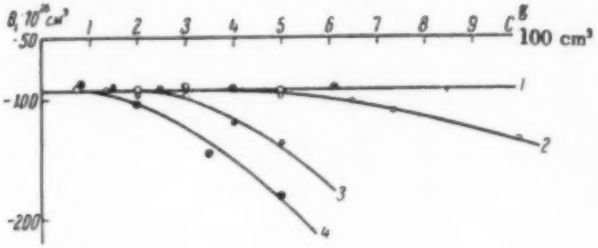


FIG. 1. Dependence of birefringence value on acceleration for solutions of two polystyrene fractions: (a, b) (fr. 1) and (c, d) (fr. 1[a]) in dioxane; (e) in bromoform (fr. 1). The numbers indicated on the straight lines show the solution concentration in g/100 cm².

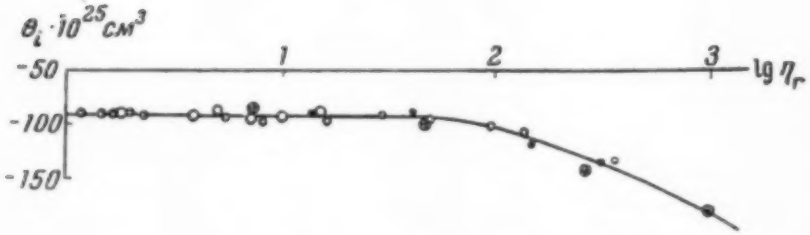
In the work [9] it was pointed out that in the concentration range, studied previously, for the polystyrene-bromoform system, the θ_i value can be determined by Equation [5] from the data of birefringence and viscosity for solutions of any concentration and any molecular weight.

Fig. 2. *a* demonstrates the dependence of θ_i values on concentration for all solutions studied of four polystyrene fractions in bromoform.

As is apparent from the diagrams, for low molecular specimen (VI fraction) θ_i retains a constant value in the whole concentration range studied. However, for higher molecular specimens, this constancy is disturbed, and the smaller the solution concentration, the higher the molecular weight of the fraction.



a



b

FIG. 2. Dependence of θ_i natural macromolecular anisotropy; (a) on solution concentration for four polystyrene fractions (calculated by equation 5): ○ — VI fr.; ● — I fr.; ⊙ — I^b fr.; ⊕ — I^a fr. (b) on logarithm of relative solution viscosity for five polystyrene fractions: ○ — VI fr.; ○ — I fr.; ○ — I^b fr.; ⊕ — I^a fr.; ◑ — V fr. 92×10^{25} cm³.

From Fig. 2. *b* it is apparent that the disturbance of θ_i constancy is determined only by relative solution viscosity, regardless of the concentration and molecular weight of the dissolved polymer.

Since the relative viscosity of the studied solutions changed by more than a factor of 10^3, we represented the dependence of θ_i on $\ln \eta_r$. The diagram shows that θ_i retains constant value for the solutions, the relative viscosity of which is not more than the value of $\eta_r < 100$. It is noted that the solutions studied earlier had a value of $\eta_r < 15$.

Thus the correctness of our calculations regarding hydrodynamic interaction of macromolecules for sufficient wide concentration range (relative viscosities) is confirmed [1, 2, 9, 14]. Nevertheless, the empirical formula [4] has a restricted application and cannot be used for all the concentration ranges studied in this work.

Peterlin developed a semi-empirical theory of dynamic birefringence in concentrated solutions, with no shape effect [15, 16]. According to this theory, Δn birefringence value can be expressed as follows:

$$\Delta n = \frac{4\pi}{45kT} \times \frac{(n_s^2+2)^2}{n_s} (\alpha_1 - \alpha_2)\, g\,(\eta - \eta_0) \tag{9}$$

Here η is the solution viscosity, the remaining symbols have the meanings* already shown.

Equation [9] shows that dependence of Δn on $g(\eta - \eta_0)$ should be represented lineally, the slope of the line making it possible to determine $(\alpha_1 - \alpha_2)$ or θ_i.

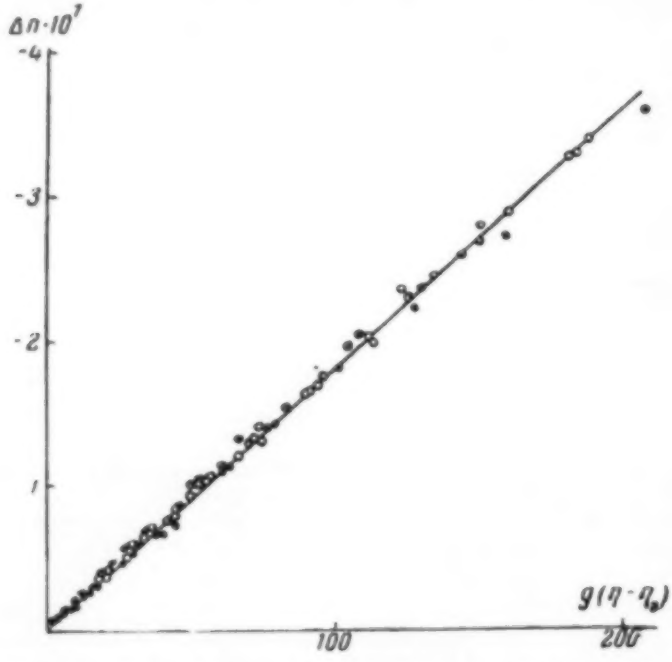


FIG. 3. Function of $\Delta n = f[g(\eta - \eta_0)]$ for four polystyrene fractions in bromoform.

This relation is very well confirmed by our experimental data. Δn values for all concentrations, all fractions and all studied speed gradients are shown on one line (Fig. 3).

* In determination of η we used the same acceleration ranges as also in measuring Δn.

More detailed analysis of experimental data can be made, if we write Equation [9] in the form of Equation [5] (in conditions of $g \to 0$):

$$\frac{\Delta n}{g(\eta - \eta_0)} \times \frac{3n_s kT}{4\pi} \left(\frac{3}{n_s^2 + 2} \right)^2 = \theta_i \tag{10}$$

representing the dependence of θ_i values, calculated according to Equation [10] on lg η_r (Fig. 4).

From the diagram it is apparent that θ_i retains a constant value for all concentrations, studied here, for which relative viscosity varies more than by a factor of 1000.

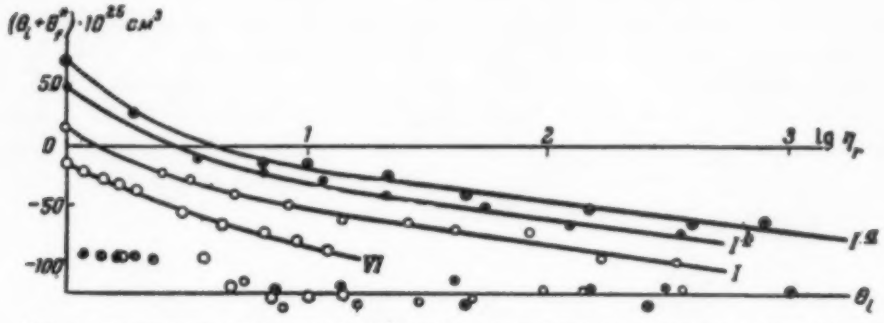


FIG. 4. Dependence of θ_i and $(\theta_i + \theta_f^*)$ values, calculated by equations 10 and 11 on the logarithm of relative solution viscosity. The fraction numbers are indicated by the curves. On θ_i curve: ○ — VI fr.; ○ — I fr.; ● — I^b fr.; ⊕ — I^a fr.; ◑ — V fr. (measured earlier) 122×10^{25} cm³.

This circumstance is particularly essential at the study of macromolecules, the natural anisotropy of which is very small. Here θ_i can be determined from the data given for great concentrations, which in this case are easier to study.

It is true, that θ_i values, calculated by Equation [10] prove to be somewhat larger than θ_i calculated by Equation [5] for the range when $\eta_r \leqslant 100$. The last values coincide with those calculated under conditions when $c \to 0$. Only the first two points, for which $\eta_r \leqslant 3$, give very close values of θ_i, when calculating them according to Equations [5] and [10].

When $\eta_r \to 1$, formulae [5] and [10] are equivalent. This equivalence is approximately retained until $\eta_r \approx 3$. In this range θ_i, calculated according to Equation [10], increases very slightly. When $\eta_r \geqslant 3$, θ_i becomes constant, which in the course of further large changes of η_r remains constant.

Since in this work sufficiently concentrated polystyrene solutions were studied in bromoform, there are few points in the small relative viscosity range. Therefore we used the experimental data previously obtained by one of the authors for solutions of V polystyrene fraction ($M = 2{\cdot}85 \times 10^5$) in bromoform. (These measurements were carried out by means of an instrument with external rotor and working length of $l = 10$ cm).

The initial points of Fig. 4 verify that θ_i, calculated by Equations [5] and [10], have in this range very close values.

If we determine $\theta_i+\theta_f^*$ by Equation [6] the alteration of this value together with the solution concentration will at first be determined only by θ_f^* variation, but at significant concentrations ($\eta_r \geqslant 100$) θ_i will begin to change as well.

If we calculate hydrodynamic interaction of macromolecules according to Peterlin's theory, Equation [6] can be rewritten as follows:

$$\frac{\Delta n}{g(\eta-\eta_0)} \times \frac{3n_s kT}{4\pi}\left(\frac{3}{n_s^2+2}\right)=\theta_i+\theta_f^* \tag{11}$$

In Fig. 4 we represented dependence of $(\theta_i+\theta_f^*)$ values, calculated according to Equation [11], on $\lg\eta_r$. Diagrams show that with increase of solution concentration the total anisotropy of macromolecules approaches the value of θ_i natural anisotropy.

Apparently $(\theta_i+\theta_f^*)$ curves should converge asymptotically to the curve, characterizing θ_i value. Therefore the problem on the possibility of obtaining a solution, in which no shape effect is present, should be solved experimentally by studying even more concentrated solutions.

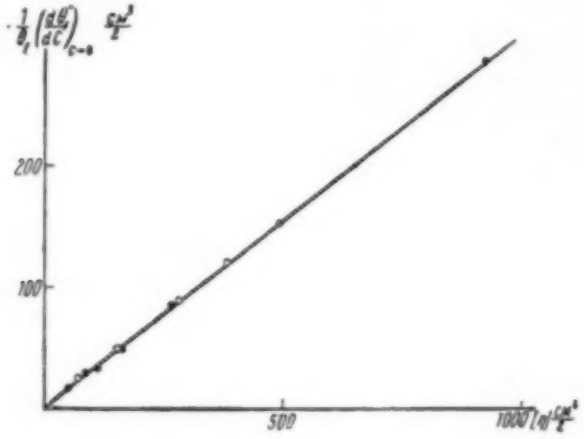


FIG. 5. Function of $-\frac{1}{\theta_f}(d\theta_f^*/dc)_{c\to 0}=f([\eta])$ for eleven polystyrene fractions in dioxane.

In any case, on the basis of the experimental data given, it is possible to conclude that when studying the deformation birefringence in swollen polymers, the shape effect should be absent irrespective of the solvent used.

In small concentration range, the conclusions drawn in earlier works [7–9] are verified. Thus the dependence to be determined by Equation [8], is given in Fig. 5. Here, the data given for polystyrene fractions in dioxane, obtained earlier [8, 9] and in this work, are represented. All points lay well on one line.

Other examples, belonging to the small concentration range, we will not discuss to avoid overloading the present exposition.

We take the opportunity to express our sincere gratitude to V. N. Tsvetkov for the valuable discussion in respect of the explained problems.

CONCLUSIONS

(1) During work it was established that the earlier indicated [1, 9] calculation of hydrodynamic interaction of macromolecules is correct for a high concentration range, but has limited application. The limitation is determined only by relative solution viscosity, regardless of its concentration, and the molecular weight of the dissolved polymer.

(2) The calculation of hydrodynamic interaction for the system studied, carried out according to Peterlin's theory [15, 16], proved to be suitable for all solutions studied, in which the relative viscosity altered more, than by a factor of 1000.

(3) The study of shape effect in the polystyrene-dioxane system verify the correctness of our formula [9] for the calculation of optical interaction of macromolecules in range of limited concentrations.

(4) In the most concentrated solutions the total macromolecular anisotropy has a value, close to its natural anisotropy. Experimental data makes it possible to prove that in swollen polymer the shape effect is absent, regardless of the refractive index of the solvent applied.

Translated by E. SEMERE

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POLYMERIZATION OF MIXED ARYL (ALKYL) *CYCLO*TETRASILOXANES*

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(*Received* 24 *November* 1959)

ONE of the methods of synthesis of high-molecular linear or branched polyorganosiloxanes, other than hydrolysis of bifunctional alkyl- or arylhalogenosiloxanes, is the polymerization of cyclic compounds with acid and basic catalysts [1–4]. Polymerization of cyclic compounds, however, has been studied very little. The literature available relates only to catalytic polymerization of octamethyl*cyclo*tetrasiloxane, which is the basic monomer for obtaining polydimethylsiloxane rubber. Polymerization of octamethyl*cyclo*tetrasiloxane under the effect of sulphuric acid was studied by Kozima [5], who showed that the rate of polymerization increases linearly with sulphuric acid concentration. The author assumes that the process consists of step-by-step condensation of hydroxyl-containing products, formed by opening of rings. Stavitskii [6] and his fellow workers studied the polymerization of octamethyl*cyclo*tetrasiloxane, using sulphuric acid, phosphoric anhydride, *ortho*phosphoric acid, aluminium chloride, ferric chloride, iron sulphate, and aluminium sulphate as catalysts and found that these catalysts result in polymerization. It is well-known that cyclic compounds, containing phenyl groups on the silicon atom, e.g. triphenyltrimethyl*cyclo*tetrasiloxane, polymerize with difficulty.

In this connection, the study of the effect of phenyl groups in cyclic tetrasiloxanes on their ability to undergo catalytic polymerization is of great interest.

In this work some experimental data are discussed relating to catalytic polymerization of mixed alkyl (aryl)- *cyclo*-siloxanes. For this purpose we synthesized heptamethylphenyl*cyclo*tetrasiloxane, hexamethyldiphenyl*cyclo*tetrasiloxane and heptamethylchlorophenyl*cyclo*tetrasiloxane and heptamethylchlorophenyl*cyclo*tetrasiloxane. These compounds were obtained by joint hydrolysis of two different bifunctional monomers with water in acid medium.

$$n\mathrm{R_2SiCl_2}+m\mathrm{RR'SiCl_2}+(n+m)\mathrm{H_2O}\rightarrow(\mathrm{R_2SiO})n(\mathrm{RR'SiO})m+2(n+m)\mathrm{HCl}.$$

Properties of the compounds obtained are indicated in Table 1.

Polymerization of these cyclic compounds was effected as follows. In a graduated test tube, fitted with a stirrer, the monomer was accurately measured and catalyst (sulphuric and ethylsulphuric acid) added. The test tube was placed

* Vysokomol. soedin. **1**: No. 4, 613–618, 1959.

in an thermostat accurate to $\pm 0{\cdot}1$°C. After completion of polymerization, the content of the test tube was diluted by benzene, rinsed with water, and dried with $CaCl_2$. After this, the benzene solution was decanted into a weighed retort, from which at first benzene, and later monomer was distilled at 7 mm residual pressure. The polymer yield was determined by the weight of polymer and distilled monomer.

TABLE 1. PHYSICAL PROPERTIES OF *CYCLO*SILOXANES

Name of material	Boiling point in °C (mm);	d_4^{20}	MR_D		η_{20} centi-Stokes values
			Found	Calculated	
Heptamethylphenyl-*cyclo*tetrasiloxane	115–117 (7)	1·0163	94·59	94·36	6·16
Hexamethyldiphenyl-*cyclo*tetrasiloxane	167–168 (7)	1·0602	113·58	113·94	16·47
Heptamethylchloro-phenyltetrasiloxane	150 (18)	1·0882	97·88	98·50	10·49

It was observed that, at a catalyst concentration higher than 2 per cent by weight, and with continuous heating, insoluble polymer forms. This is apparently connected with the partial breakdown of polymer at Si—C_6H_5 bond, with the formation of three-dimensional structure. During the interaction of *cyclo*siloxanes with concentrated sulphuric acid and ethylsulphuric acid, opening of rings occurs,

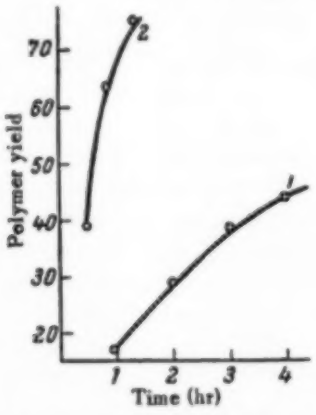


FIG. 1. Polymerization of heptamethylphenyl*cyclo*tetra-siloxane in the presence of: (1) ethylsulphuric acid; (2) sulphuric acid.

with further polymerization to high molecular compounds. The ring opening rate and initial increase of polymer depend on the nature of the catalyst, the concentration of acid and reaction temperature. At the same temperature sulphuric acid catalyzes polymerization several times faster than ethylsulphuric acid (Figure 1).

Analogous results were obtained with polymerization of hexamethyldiphenyl-*cyclo*tetrasiloxane and heptamethylchlorphenyl*cyclo*tetrasiloxane. For soluble polymers infra-red spectra were observed. Frequencies were found, characteristic for $Si-CH_3$(1429 cm^{-1} and 800 cm^{-1}) and $Si-C_6H_5$(1429 cm^{-1}) bonds. The intensity of the bond coincides with that of the monomer, which can indicate the absence of processes leading to splitting-off of phenyl radicals from silicon atoms during polymerization (Figure 2).

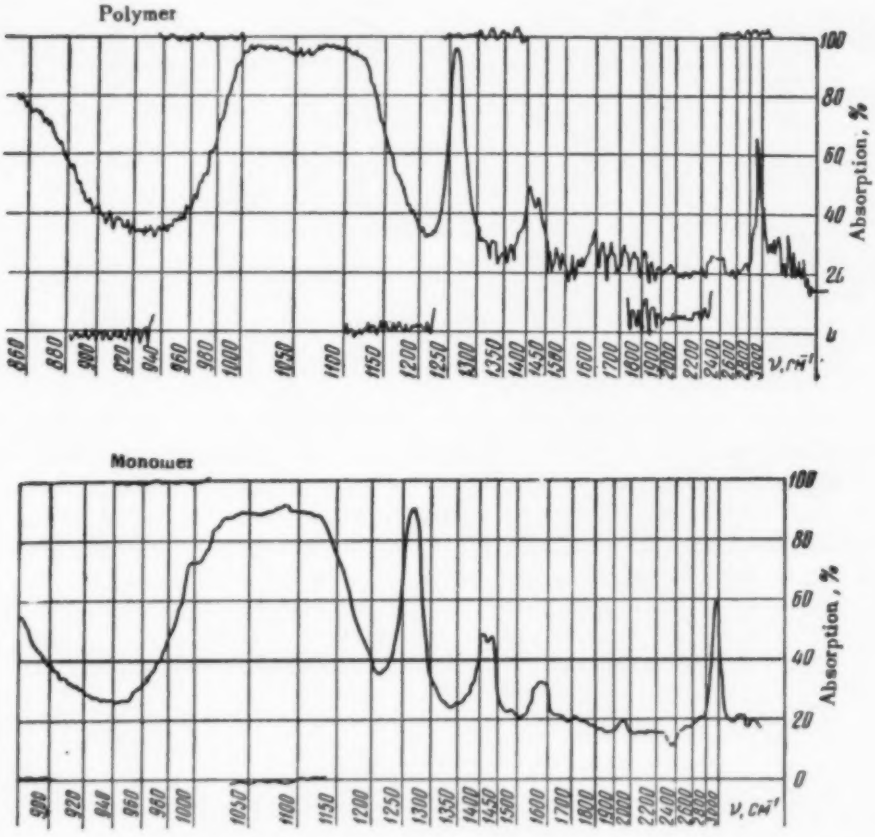


FIG. 2. Infra-red spectra of heptamethylphenyl*cyclo*tetra-siloxane and a polymer obtained from heptamethyl*cyclo*tetra-siloxane in the presence of ethylsulphuric acid.

No hydroxyl groups were detected.

The ring opening and polymerization rate of heptane thylphenyl*cyclo*tetrasiloxane are different. During the same polymerization time, e.g. 5 hr, the amount of polymer obtained from heptamethyl*cyclo*tetrasiloxane, reached 52 per cent, that from heptamethylchlorophenyl*cyclo*tetrasiloxane, 45 per cent, and from

hexamethyldiphenyl*cyclo*tetrasiloxane, 41 per cent; i.e. decrease of polymerization rate is observed depending on the number of phenyl groups in the ring and on the introduction of a chlorine atom into the phenyl group (Figure 3).

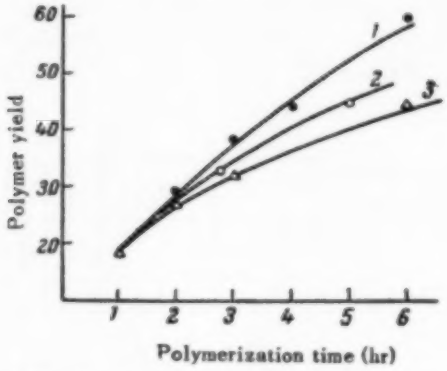


FIG. 3. Variation of polymerization rate with monomer structure. (1) Heptamethylphenyl*cyclo*tetrasiloxane (2) Heptamethylchlorophenyl*cyclo*tetrasiloxane (3) hexamethyldiphenyl*cyclo*tetrasiloxane.

Heptamethylphenyl*cyclo*tetrasiloxane polymerization was studied at different temperatures. The principal kinetic data were obtained with a maximum polymerization yield of 70 per cent at different catalyst concentrations. Determination of reaction order showed that the reaction takes place according to a monomolecular mechanism. The rate constants, calculated according to the first order equation, remained constant during the reaction. The dependence of the reaction rate constants on temperature and catalyst concentration are shown in Table 2.

TABLE 2. VARIATION OF POLYMERIZATION RATE CONSTANT OF HEPTAMETHYLPHENYL*CYCLO*TETRASILOXANE WITH TEMPERATURE AND CATALYST CONCENTRATION

Ethylsulphuric acid concentration 1·78 weight %		Polymerization temperature 96°C	
polymerization temperature (°C)	K, mole/l. min	ethylsulphuric acid concentration weight (%)	K, mole/l. min
96	0·00273	1·78	0·00273
90	0·000510	0·55	0·00187
80	0·000278		

Activation energy is 35·5 kcal/mole.

During polymerization in presence of sulphuric acid, it was shown that the polymer yield is proportional to the catalyst concentration (Fig. 4).

The kinetic curves (Fig. 3) are characteristic of the slow monomolecular course of polymerization.

All polymers obtained are easily soluble in benzene and toluene. Molecular weights of fractionated and unfractionated polymers were determined. Fractionation of polymers, obtained by polymerization of heptamethylphenyl*cyclo*tetra-

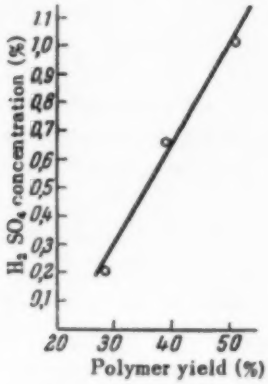


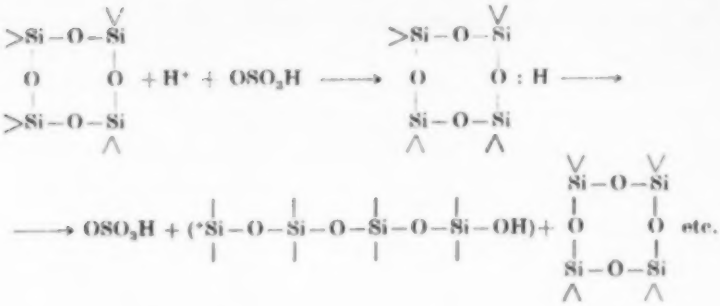
FIG. 4. Variation of polymer yield with catalyst concentration (polymerization time is 30 min).

siloxane and hexamethyldiphenyl*cyclo*tetrasiloxane, was carried out by fractional precipitation from 5% benzene solution with methanol [7] at 20°C, and was found that the fractions obtained are easily soluble in these solvents. Viscosity measurements of benzene polymer solutions were carried out in a capillary viscosimeter, for volatile liquids at 20°C. The results obtained are indicated in Table 3.

From the experimental data it is apparent that the intrinsic wiscosities increase with polymerization time. This shows that, at the beginning of polymerization, polymers develop with molecular weight which is lower than those formed at the end of the reaction. The influence of polymerization time on the average molecular weight indicates a gradual increase of polymer molecules. Molecular weight values of polymers of heptamethylphenyl*cyclo*tetrasiloxane are shown in Table 4.

Molecular weight was calculated by the formula, given for polydimethylsiloxane rubber [8] $[\eta]=2{\cdot}15\times10^{-4}\ M^{0{\cdot}65}$. There is a sufficient basis for the use of the K_m and α numerical values found for polydimethylsiloxane rubber, since one phenyl group can hardly have a greater influence on the rigidity of the chain than seven methyl groups in the heptamethylphenyl*cyclo*tetrasiloxane polymer chain.

On the whole the fission of *cyclo*siloxane molecules with sulphuric, or ethylsulphuric acid can be represented by the following scheme:



The first stage is the coordination of proton with the oxygen of siloxane group of the ring and then breaking of the ring with formation of a complex ion. The growth of the chain probably occurs as a result of interaction of the active centre

TABLE 3. THE INFLUENCE OF POLYMERIZATION TIME ON [η] VALUE

Polymer from heptamethylphenyl*cyclo*tetrasiloxane				Polymer from hexamethyldiphenyl*cyclo*tetrasiloxane			
Polymerization time (hr)	Catalyst	Polymer yield (%)	[η]	Polymerization time (hr)	Catalyst	Polymer yield (%)	[η]
2	Ethylsulphuric acid	30·0	For 1 fraction 0·14	2	Ethylsulphuric acid	27·8	0·05
2	,, ,,		For 2 fractions 0·09	5	,, ,,	44·6	0·17
6	,, ,,	60·0	For 1 fraction 0·50	6	,, ,,	—	For 1 fraction 0·136
6	,, ,,		For 2 fractions 0·25	6	,, ,,	—	For 2 fractions 0·12
4	,, ,,	44·1	0·10	6	,, ,,	—	For 3 fractions 0·08
9	,, ,,	75·9	0·456	—	—	—	—
0·5	Sulphuric acid	52·5	0·45	—	—	—	—
5	,, ,,	—	0·97	—	—	—	—

with the monomer molecules, although the other possibility—reaction of active centre with activated monomer molecules—should not be overlooked either. In catalytic polymerization the break of the chain results in the loss of activity, i.e.

loss of ability of the end groups to join the molecules of the monomer. This occurs as a result of loss of catalyst from the end of the growing chain and stabilization of the product obtained.

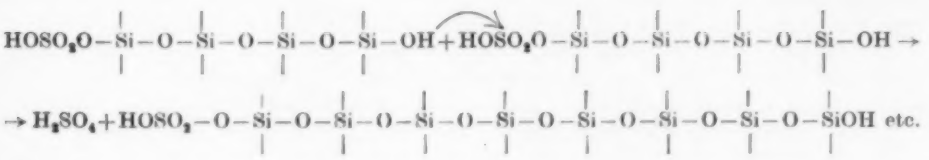


TABLE 4. AVERAGE MOLECULAR WEIGHT OF HEPTAMETHYLPHENYL*CYCLO*TETRASILOXANE POLYMER IN RELATION TO POLYMERIZATION TIME AND NATURE OF CATALYST

Polymerization time (hr)	Catalyst	Polymer yield (%)	Molecular weight
2	Ethylsulphuric acid	44·1	21,280
9	As above	75·9	130,000
0·5	Sulphuric acid	52·2	128,200
5	As above	—	418,800

It is well-known that condensation at the expense of hydroxyl groups situated at the ends of the polymer chain of polyorganosiloxanes takes place with great difficulty when the number of these groups is not great. In case of the heptamethylphenyl*cyclo*tetrasiloxane polymer the number is so small that with ordinary analytical methods, and even by means of infra-red spectra its determination was not possible. Thus, the hypothesis expressed by Kozima concerning the mechanism of polymerization of octamethyl*cyclo*tetrasiloxane by means of gradual condensation of hydroxyl-containing products, forming during opening of the ring, is not very well-founded. There is every reason to suggest that the most correct mechanism is one of stepwise polymerization.

CONCLUSIONS

(1) It was found that mixed aryl (alkyl)-*cyclo*tetrasiloxanes polymerize in the presence of acid catalysts with formation of soluble polymers.

(2) It was proved that with the introduction of halogen atoms in the phenyl group and with increase of number of phenyl groups in the ring, the polymerization rate decreases.

(3) It is suggested that alkyl (aryl)-*cyclo*tetrasiloxanes polymerize according to a stepwise mechanism through the intermediate formation of the siliconium ion.

Translated by E. SEMERE

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CARBOHYDRATE POLYMERS AND COPOLYMERS—XIV. COPOLYMERIZATION OF ETHYLENE WITH UNSATURATED COMPOUNDS IN THE PRESENCE OF ALKYL BORON COMPOUNDS*

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(*Received* 4 *March* 1959)

EARLIER [1] there was an indication of the possibility of obtaining copolymers of ethylene with styrene, acrylonitrile, methylmethacrylate and vinyl acetate in the presence of tributylboron as polymerization catalyst.

In this paper the results are discussed of studying copolymerization of ethylene with acrylonitrile, vinyl chloride and styrene in the presence of tri*iso*butylboron as catalyst †. The experiments were carried out in a rotating autoclave at 100 atm pressure of ethylene and a temperature from 18°C (initial temperature) to 50°C (final temperature). Studies were also carried out at lower initial pressure and lower initial temperature. With the preliminary experiments it was established that in the copolymerization reaction of ethylene with other monomers, ~ 20 per cent of the ethylene takes part, the remainder is in gaseous phase and is used up in forming an ethylene solution in the solvent; in calculations of the composition of initial monomer mixture this was taken into consideration.

In order to explain the effect of tri*iso*butylboron concentration on the copolymerization of ethylene with acrylonitrile, studies were carried out, in which the molar ratio of "ethylene : acrylonitrile" was constant and equal with 80 : 20, the reaction temperature was the same (as indicated above), the duration of reaction was 24 hr. "Benzine-rubber" served as solvent, the quantity of which was kept constant, and the catalyst concentration altered from 1 to 4 per cent by weight of solvent. Copolymers of ethylene with acrylonitrile are soluble only in dimethylformamide and therefore they were purified by re-precipitation with methyl alcohol from solutions in dimethylformamide. The precipitated copolymer was boiled for a few hours with methyl alcohol, filtered off and dried in vacuum at 50°C to constant weight. The composition of the copolymers obtained was determined by analysis of nitrogen content.

* Vysokomol. soedin. 1: No. 4, 627–634, 1959

† The authors express their gratitude to A. F. Zhigach for supplying tri*iso*butylboron.

From Table 1 it is apparent that by increasing the catalyst concentration from 1 to 2 per cent by weight, the copolymer yield increases from 10 to 25·5 per cent; further increase of catalyst concentration give a somewhat decreased yield. In accordance with the results obtained, all subsequent experiments were carried out at a tri*iso*butylboron concentration of 2 per cent by weight of solvent. The copolymer composition and the temperature of vitrification do not change substantially when the catalyst concentration is varied. In Fig. 1 thermomechanical curve of a copolymer is shown, which was obtained with 2 per cent catalyst. The results indicated on Table 1 show as well that, in spite of the fourfold (against the equimolecular ratio) ethylene excess, copolymers contain more acrylonitrile than ethylene. This indicates greater relative activity of acrylonitrile in comparison with ethylene.

TABLE 1. COPOLYMERIZATION OF ETHYLENE WITH ACRYLONITRILE

Catalyst quantity, wt. — % of the solvent	Copolymer yield (wt. — %)	Nitrogen content in the copolymer (wt. — %)	Copolymer contains (mol. %)		Vitrification temperature (°C)
			Acrylonitrile	Ethylene	
1·0	9·9	21·11 21·25	68·5	31·5	70
2·0	25·5	22·59 22·67	76·5	23·5	62
3·0	18·3	21·41 21·12	68·5	31·5	67
4·0	16·0	22·53 22·70	76·5	23·5	66

In order to explain the effect of reaction temperature on the copolymer yield of ethylene with acrylonitrile, and on copolymer properties, a series of experiments was carried out, in which all conditions (nature and volume of solvent, reaction time and catalyst concentration) were the same, and the reaction temperature varied.

The effect of temperature was inspected at different "ethylene : acrylonitrile" ratios; the experimental conditions and the results obtained are shown on Table 2.

In Table 2 it is apparent that the reduction of initial polymerization temperature from 18 to —70°C results in an increase of ethylene content in copolymer, approximately by a factor of 2, with an "ethylene : acrylonitrile" ratio of 80 : 20 in the initial mixture. Where there is a smaller ethylene content in the initial monomer mixture, the reduction of initial reaction temperature does not practically effect the copolymer composition. In all cases the reduction of initial

polymerization temperature results in an increase of copolymer yield. The vitrification temperature of the copolymers obtained does not depend on the reaction temperature and is within the range of 60–65°C.

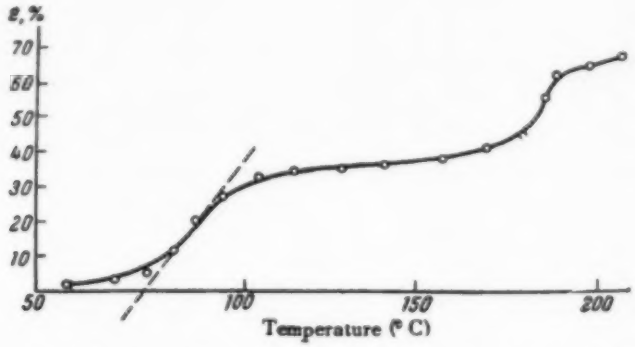

FIG. 1. Thermomechanical curve of copolymer of ethylene with acrylonitrile.

TABLE 2. COPOLYMERIZATION OF ETHYLENE AND ACRYLONITRILE AT DIFFERENT TEMPERATURES

Molar ratio of ethylene acrylonitrile	Reaction temperature		Copolymer yield (weight %)	Nitrogen content in copolymer (weight %)	Copolymer contains (mol %)		Vitrification temperature (°C)	$[\eta]$
	Initial	Final			Ethylene	Acrylonitrile		
80 : 20	18	50	15·0	22·67 22·59	23·5	76·5	62	0·48
80 : 20	−70	18	20·6	18·63 18·59	43·8	56·2	65	0·18
80 : 20	−70	50	18·6	18·54 18·43	44·4	55·6	64	0·17
40 : 60	18	50	40·0	24·65 24·49	15·5	84·5	63	0·23
40 : 60	−70	18	44·0	23·59 23·53	19·3	79·7	62	—
20 : 80	18	50	39·4	23·20 23·08	21·2	78·8	60	0·19
20 : 80	−70	18	63·8	23·91 24·13	15·2	84·8	62	—

Note. 1. Triisobutylboron concentration − 2 wt. − % of the solvent; solvent − "benzene-rubber", polymerization time − 24 hr. 2. The characteristic viscosity values, shown in Tables 2 − 4 were determined by solution viscosity measurement in dimethylformamide at 25° C.

In order to explain the effect of the ethylene/acrylonitrile ratio in the initial mixture on the copolymer yield and properties, two series of experiments were

carried out, in which all conditions, except the "ethylene : acrylonitrile" ratio were the same. The conditions of these experiments and the results obtained are indicated in Table 3 and Fig. 2 and 3.

TABLE 3. COPOLYMERIZATION OF ETHYLENE AND ACRYLONITRILE

Molar ratio of ethylene: acrylonitrile	Copolymer yield (wt. – %)	Nitrogen content in copolymer (wt. – %)	Copolymer contains (mol. %)		Vitrification temperature (°C)	$[\eta]$
			Ethylene	Acrylonitrile		
	Initial temperature 18°C, final temperature 50°C					
80 : 20	15·0	22·59 22·67	23·5	76·5	62	0·48
40 : 60	40·0	24·65 24·49	15·5	84·5	63	0·23
20 : 80	39·4	23·20 23·08	21·2	78·8	60	0·19
	Initial temperature –70°, final temperature 18°C					
80 : 20	20·6	18·63 18·59	43·8	56·2	70	0·18
60 : 40	41·6	23·03 23·09	21·2	78·8	63	0·35
40 : 60	44·0	23·59 23·53	19·3	80·7	62	—
20 : 80	63·8	23·91 24·13	15·2	84·8	62	—

Note. Triisobutyl concentration – 2 wt. – % of the solvent, solvent – "benzene-rubber", reaction time 24 hr.

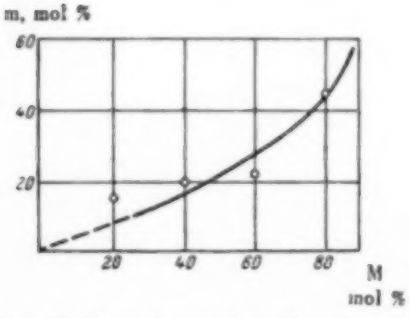

FIG. 2. Dependence of copolymer composition of ethylene with acrylonitrile on the ratio of initial components. (M) Ethylene content in the initial mixture (m) Ethylene content in copolymer.

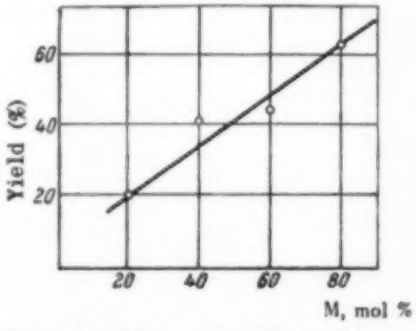

FIG. 3. Dependence of yield of copolymer of ethylene with acrylonitrile on the ratio of initial components. (M) Acrylonitrile content in the initial mixture.

From Table 3 and Fig. 3 it is apparent that the increase of acrylonitrile content in initial monomer mixture results in an increase of copolymer yield

and acrylonitrile residue content in the copolymer. This is in accordance with the indicated higher relative activity of acrylonitrile in copolymerization with ethylene. The vitrification temperature of copolymer does not depend on the ratio of initial materials. When polymerization is carried out at lower temperatures, the higher relative activity of acrylonitrile persists, as Table 3 and Fig. 2 indicate. The vitrification temperature, when increasing the ethylene residue content in the copolymer to 43·8 per cent, rises to 70°C. Copolymer, containing 43·8 mol. per cent ethylene residue, in contrast to other copolymers of ethylene with acrylonitrile, fuses without decomposition. The fusible copolymer of ethylene with acrylonitrile, has been characterized in more detail than the other copolymers obtained from ethylene with acrylonitrile; the properties of this copolymer are shown in Table 4, and a thermomechanical curve is given in Fig. 4.

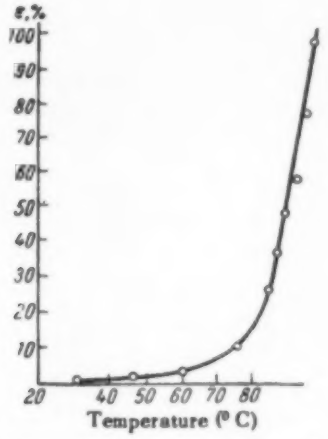

FIG. 4. Thermomechanical curve of fusible copolymer of ethylene with acrylonitrile.

It is interesting to note that irrespective of polymerization in solution, the copolymer obtained is of high molecular weight.

In order to explain the effect of the nature of solvent on the yield of copolymer and its composition, two experiments were carried out under the same conditions, except that in one of the experiments, "benzene-rubber", and in the other toluene was used as solvent. Catalyst (tri*iso*butylboron) concentration was 2 per cent by weight of the solvent, reaction time was 24 hr, initial temperature 70°C, final temperature 18°C, molar ratio of ethylene : acrylonitrile was 60 : 40.

The results of experiments are shown in Table 5. As Table 5 indicates, replacement of mixture of aliphatic hydrocarbon solvents by aromatic ones, does not lead to any change in composition and yield of copolymer.

Preliminary experiments established that vinyl chloride polymerizes in the presence of tri*iso*butylboron when toluene is used as solvent.

Copolymerization of ethylene with vinyl chloride was carried out by a similar method to that used for ethylene and acrylonitrile at low temperatures. Tri-

TABLE 4. PROPERTIES OF FUSIBLE COPOLYMER OF ETHYLENE WITH ACRYLONITRILE

Characteristic viscosity (25°, dimethylformamide)	0·18
Molecular weight (diffusion of light)	910,000
Solubility	Soluble only in dimethylformamide
Roentgen ray analysis	Characteristic feature is the high regularity inside the sections of the chain. Evidence of crystallinity is observed
Vitrification temperature (°C)	70
Fusion temperature (°C)	96–98
Specific gravity	1·0855
Equilibrium hydrophilic nature	0·2%
Inflammability	After withdrawal from the flame, burning ceases
Ability to form fibres	Fibres formed by fusion

TABLE 5. COPOLYMERIZATION OF ETHYLENE AND ACRYLONITRILE IN DIFFERENT SOLVENT

Solvent	Copolymer yield (wt. —%)	Nitrogen content in the copolymer (wt. —%)	Copolymer contains (mol. %)	
			Ethylene	Acrylonitrile
"Benzene-rubber"	31·7	21·45 21·50	30·0	70·0
Toluene	32·4	21·65 21·79	28·5	71·5

*iso*butyl concentration was 2 per cent by weight of toluene. Copolymer composition was calculated from the chlorine content of the copolymer. The results of the experiments are indicated in Table 6 and Fig. 5 and 6.

As Table 6 and Fig. 5 indicate, copolymers of ethylene with vinyl chloride contain more ethylene residues than the initial monomer mixtures. This shows great relative activity of ethylene in copolymerization with vinyl chloride; in accordance with this, an increase in copolymer yield is observed with an increase of the more active monomer (ethylene) content in the initial mixture (see Fig. 6). The composition of copolymers affects their properties. As Table 6 indicates, an increase of content of ethylene links in copolymer above 40 per cent results in an increase of the vitrification temperature of copolymer and decrease of

TABLE 6. COPOLYMERIZATION OF ETHYLENE WITH VINYL CHLORIDE

Molar ratio of ethylene vinyl chloride	Copolymer yield (wt. — %)	Chlorine content in copolymer (wt. — %)	Copolymer contains		Vitrification temperature (°C)	Note
			Ethylene	Vinyl chloride		
80 : 20	56·8	12·79 12·88	88·1	11·9	57	Copolymer is white, waxy, at 70°C develops 1% solutions in toluene, dichlorethene, tetralin.
60 : 40	48·9	22·69 22·78	77·2	22·8	30	Copolymer is white, pasty, forms 1% solutions in toluene (at 18°C), in dichlorethane (at 40°C) and tetraline (at 40°C).
40 : 60	55·0	33·66 33·79	60·3	39·7	—50	Copolymer is transparent, viscous, develops 1% solutions at 18°C in toluene, and dichlorethane, and at 40° in tetraline.
20 : 80	40·5	41·56 41·51	44·7	55·3	—5	Copolymer is white, elastic, forms 1% solutions at 18°C in toluene and dichlorethane, and 40°C tetralin.

Note. Reaction time is 24 hr, initial temperature is —70° C, final temperature 18° C.

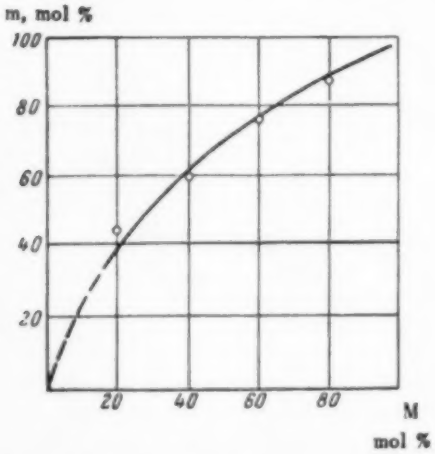

FIG. 5. Dependence of composition of copolymer of ethylene with vinyl chloride on the ratio of initial components. (M) Ethylene content in the initial mixture (m) ethylene content in copolymer.

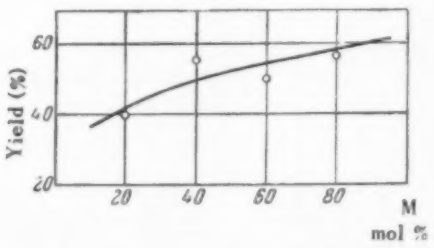

FIG. 6. Dependence of yield of copolymer of ethylene with vinyl chloride on the ratio of initial components. (M) Ethylene content in the initial mixture.

solubility in organic solvents; this is particularly noticeable when using dichlorethane as solvent. Determination of molecular weight of a copolymer, containing 44·7 per cent mol. per cent ethylene residues by a method of light scattering showed that the copolymer is a high-molecular compound, with a molecular weight of 142,000. In Fig. 7 a and b thermomechanical curves are shown of two copolymers of ethylene with vinyl chloride. It is interesting to note the emergence of elastic properties of copolymers of ethylene with vinyl chloride, forming inflexible homopolymers. Apparently, in the given case intramolecular plasticization takes place as a result of the abrupt disturbance of the regularity of the polymer chain structure and decrease in density of packing of the polymer chains. X-ray analyses of copolymer, containing 22·8 mol. per cent vinyl chloride residues, showed that it was a crystalline polymer with the same degree of regularity of chain molecules as polyethylene.

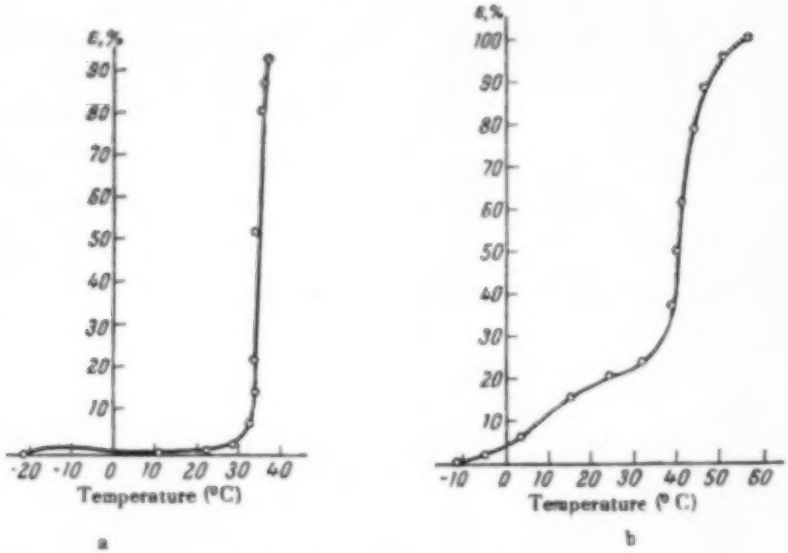

FIG. 7. Thermomechanical curve of copolymer of ethylene with vinyl chloride: (a) 22·8 mol. % ethylene; 77·2 mol. % vinyl chloride (b) 44·7 mol. % ethylene, 55·3 mol. % vinyl chloride.

The results obtained in copolymerization of ethylene with styrene, in conditions similar to that of copolymerization of ethylene with vinyl chloride, are indicated in Table 7. Toluene was used as solvent in the reaction; catalyst concentration was 2 per cent by weight of the solvent, the initial temperature —70°C, final temperature 18°C, reaction time 24 hr. All the copolymers obtained are easily soluble in toluene, dichlorethyne, and tetralin at room temperature. The composition of the copolymers obtained was calculated from the carbon content.

As Table 7 indicates, copolymerization of ethylene with styrene takes place with considerably greater difficulty than copolymerization of ethylene with acrylonitrile, or vinyl chloride. The low copolymer yield can be explained by the fact that styrene is a more active monomer, which polymerizes with difficulty in toluene solution in the presence of alkyl compounds of boron, as this was established earlier [2]; the behaviour of more active monomer determines

TABLE 7. COPOLYMERIZATION OF ETHYLENE WITH STYRENE

Molar ratio of ethylene: styrene	Copolymer yield (wt. —%)	Carbon content in the copolymer (wt. —%)	Copolymer contains (mol. %)		Vitrification temperature (°C)
			Ethylene	Styrene	
80 : 20	8·0	90·23 90·12	62·5	37·5	—
60 : 40	4·8	91·46 91·64	29·0	71·0	55
40 : 60	16·6	89·51 89·46	73·8	26·2	79
20 : 80	10·5	92·13 92·09	8·2	91·8	95

the behaviour of the whole system of copolymerizing monomers. Owing to the fact that the reaction was carried out in toluene, chain transfer occurred easily as a result of interaction of the styrene radical with toluene. This should lead to both decrease in copolymer yield, and to formation of copolymer of low molecular weight. Actually, copolymer containing 91·8 mol. per cent styrene links had a molecular weight, found by method of light scattering of only 52,000.

CONCLUSIONS

(1) A study was made of the effect of different factors on the copolymerization of ethylene with acrylonitrile in the presence of tri*iso*butylboron. It was proved that acrylonitrile is of greater relative activity than ethylene in the copolymerization. Fusible copolymer was obtained, containing 44 per cent ethylene links and 56 mol. per cent acrylonitrile links.

(2) In copolymerization of ethylene with vinyl chloride, using tri*iso*butylboron, copolymers of different composition were obtained, having a wide range of properties. It was established that ethylene has a greater relative activity than vinyl chloride.

(3) A study was made of the copolymerization of ethylene with styrene in the presence of tri*iso*butylboron.

Translated by E. SEMERE

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ORGANOPHOSPHORUS POLYMERS—VI. POLYAMIDES OF SEVERAL PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS

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(*Received* 2 *February* 1959)

WE have previously studied polyamides based on *bis*-(*n*-carboxyphenyl) phenyl phosphine oxide and a number of diamines [1]. In the present work, with a view to elucidating the influence of the structure of the phosphorus-containing acids on the properties of the polyamides, we prepared and studied polyamides from several phosphorus-containing dicarboxylic acids and a series of aliphatic and aromatic diamines. Schemes illustrating the synthesis of these acids are given below. *Bis*-(*n*-carboxyphenyl) phenyl phosphine oxide was synthesized as follows:

$$C_6H_6 + PCl_3 \xrightarrow[C_5H_5N]{AlCl_3} C_6H_5PCl_2 \xrightarrow{+\,CH_3C_6H_5MgBr} (CH_3C_6H_4)_2PC_6H_5 \xrightarrow{+\,Br_2}$$

$$\longrightarrow (CH_3C_6H_4)_2P(Br_2)C_6H_5 \xrightarrow{+\,2NaOH} (CH_3C_6H_4)_2P(O)C_6H_5 \longrightarrow$$

$$\xrightarrow[H_2O+C_5H_5N]{KMnO_4} (HOOCC_6H_4)_2P(O)C_6H_5$$

The synthesis of *bis*-(*n*-carboxyphenyl) methyl phosphine and its *m* and *o* isomers is described by the scheme as under:

$$CH_3C_6H_4Br \xrightarrow{+\,Mg} CH_3C_6H_4MgBr \xrightarrow{+\,CH_3P(O)Cl_2} (CH_3C_6H_4)_2P(O)CH_3 \longrightarrow$$

$$\xrightarrow[H_2O+C_5H_5N]{KMnO_4} (HOOCC_6H_4)_2P(O)CH_3$$

The properties of the resulting compounds are reported in the experimental section.

The aliphatic diamines and the acids yielded salts in the form of light yellow powders soluble in water, methyl and ethyl alcohol and insoluble in sulphuric ether, acetone and benzene.

In common with the preparation of normal polyamides polycondensation was accomplished in test-tubes in a stream of oxygen-free nitrogen with the temperature gradually rising from 220–260°C over a period of 8 hr [2]. In the polycondensation

* Vysokomol. soedin. **1**: No. 5, 670–676, 1959.

sation reactions of aromatic diamines with phosphorus-containing dicarboxylic acids and also of the anhydride of *bis*-(*n*-carboxyphenyl) methyl phosphine oxide with aromatic and aliphatic diamines, the weighed portions of the acid and the diamine were reacted separately with a slight excess of diamine (about 5 per cent). The reaction medium needs to be thoroughly freed from air. For the first 2 hr the reaction was conducted in sealed ampoules to prevent volatilization of the diamine. Table 1 lists properties of the polyamides formed with the aliphatic diamines and Table 2 those of the polyamides formed with the aromatic diamines.

TABLE 1. PROPERTIES OF POLYAMIDES PREPARED FROM PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS AND ALIPHATIC DIAMINES

Starting components		Softening point (°C)*	Fibre-formation temperature* (°C)	Reduced viscosity $[\eta/c]_{sp}$ $c=0.5$ at 20°C
Acid	Diamine			
$C_6H_5P(O)(n\text{-}C_6H_4COOH)_2$	$NH_2(CH_2)_4NH_2$	195	228–230	0·18
,,	$NH_2(CH_2)_6NH_2$	190	230–231	0·42
,,	$NH_2(CH_2)_8NH_2$	175	190–202	0·38
,,	$NH_2(CH_2)_9NH_2$	149	173–175	0·34
,,	$NH_2(CH_2)_{10}NH_2$	150	190–192	0·38
$CH_3P(O)(n\text{-}C_6H_4COOH)_2$	$NH_2(CH_2)_4NH_2$	184	206–208	0·12
,,	$NH_2(CH_2)_6NH_2$	182	202–205	0·32
,,	$NH_2(CH_2)_8NH_2$	142	170–172	0·29
,,	$NH_2(CH_2)_9NH_2$	140	165–167	0·32
,,	$NH_2(CH_2)_{10}NH_2$	140	185–186	0·50
$CH_3P(O)(m\text{-}C_6H_5COOH)_2$	$NH_2(CH_2)_6NH_2$	134	170–172	0·36
,,	$NH_2(CH_2)_8NH_2$	133	156–158	0·30
,,	$NH_2(CH_2)_9NH_2$	124	139–141	0·34
,,	$NH_2(CH_2)_{10}NH_2$	128	153–155	0·42
$CH_3P(O)(o\text{-}C_6H_4CO)_2O$	$NH_2(CH_2)_4NH_2$	128	153–155	0·12
,,	$NH_2(CH_2)_6NH_2$	122	142–144	0·18
,,	$NH_2(CH_2)_8NH_2$	120	141–143	0·20
,,	$NH_2(CH_2)_9NH_2$	93	109–112	0·23
,,	$NH_2(CH_2)_{10}NH_2$	85	104–106	0·24

* The softening and fibre-forming temperatures were determined under a layer of paraffin. The softening temperatures found for a number of specimens from their thermal curves are in excellent agreement with the quoted values.

The polyamides are faintly coloured non-inflammable products, soluble in cresol and in both formic and acetic acids. Table 1 reveals that the softening point and the temperature at which the polyamides form fibres vary inversely with the length of the diamine carbon chain. The polyamides that contain uneven segments of η-methylene diamine have a lower fibre-forming temperature than the polyamides that have even d-methylene diamine segments, notwithstanding that the latter are longer. This phenomenon is attributed to the usual influence of the evenness or unevenness of the carbon chain.

From a comparison of the polyamides characterized respectively by the radicals C_6H_5— and CH_3— on the phosphorus atom in the acid it appeared likely that in view of the greater size of the phenyl group relative to the methyl group, the polyamides containing the methyl group would have a more loosely-packed macromolecule and thus a lower melting point (m. p.) Nevertheless the softening point and fibre-forming temperature of all the polyamides obtained from an acid with

TABLE 2. PROPERTIES OF POLYAMIDES PREPARED FROM PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS AND AROMATIC DIAMINES

Starting components		Softening point (°C)*	Fibre-forming temperature (°C)*	Reduced viscosity $[\eta_{sp}/C]_c=0{\cdot}5$ at 20°C
Acid	Diamine			
$C_6H_5P(O)$ (*n*-$C_6H_4COOH)_2$	*n*-$NH_2C_6H_4NH_2$	260	Decomposes at about 340° C	0·24
,,	*m*-$NH_2C_6H_4NH_2$	249	—	0·20
,,	*o*-$NH_2C_6H_4NH_2$	168	205–207	0·08
,,	$CH_3C_6H_3(NH_2)_2$	239	278–280	0·18
$CH_3P(O)$ (*n*-$C_6H_4COOH)_2$	*n*-$NH_2C_6H_4NH_2$	271	Softening point about 340° C	0·20
,,	*m*-$NH_2C_6H_4NH_2$	240	282–284	0,16
,,	*o*-$NH_2C_6H_4NH_2$	170	192–193	0·10
,,	$CH_3C_6H_3(NH_2)_2$	230	250–252	0·10
$CH_3P(O)$ (*m*-$C_6H_4COOH)_2$	*n*-$NH_2C_6H_4NH_2$	224	262–264	0·12
,,	*m*-$NH_2C_6H_4NH_2$	222	258–260	0·12
,,	*o*-$NH_2C_6H_4NH_2$	164	179–181	0·08
,,	$CH_3C_6H_3(NH_2)_2$	220	242–244	0·16
$CH_3P(O)$ (*o*-$C_6H_4CO)_2O$	*n*-$NH_2C_6H_4NH_2$	162	195–197	0·10
,,	*m*-$NH_2C_6H_4NH_2$	150	172–174	0·10
,,	*o*-$NH_2C_6H_4NH_2$	—	—	—
,,	$CH_3C_6H_3(NH_2)_2$	145	160–162	0·08

* Cf. table 1.

a phenyl substituent are higher than those of the polyamides obtained from acids with a methyl substituent. Clearly the key factor here is not the size of the substituent but its polarity. Thus macromolecules composed of acid radicals with a phenyl substituent have greater molecular cohesion and consequently a higher softening point and fibre-forming temperature than polymers derived from an acid with a methyl substituent on the phosphorus atom.

Polyamides which contain radicals of isomeric acid segments have different softening points and fibre-forming temperature: these are very high with polyamides containing acid segments with functional groups in the *n* position and lower with the polyamides containing acid segments with *m* or *o* configuration of the

functional groups. This is explained by the likelihood of better macromolecular packing in the case of *n* compounds than in the case of *m* and *o* acids [4]. Comparison of the results listed in Tables 1 and 2 reveals that the phosphorus-containing polyamides with aromatic diamine radicals have far higher melting points than polyamides prepared from aliphatic diamines. A possible explanation for this is the more rigid structure of the macromolecules. With this exception, as Table 2 shows, the mechanisms are the same here as in polyamides obtained from aliphatic diamines (Table 1). Hence polymers based on *n* acids have higher melting points than the polyamides from *o* acids. Polyamides based on phenyl-substituded acids melt at a higher temperature than polyamides obtained from an acid with a methyl substituent on the phosphorus. The influence of an aromatic diamine radical isomer is analogous to that of the acid radical isomer mentioned above. The insertion of the substituent (2,4-toluylene diamine) on the *m*-diamine nucleus results in all cases in a lowering of the softening point and fibre-forming temperature of the polyamides compared with the corresponding unsubstituted products synthesized from *m*-phenylene diamine.

We considered it important to compare the phosphorus-containing polyamides obtained by us with the polyamides prepared with the same diamines and dicarboxylic acids of like structure but without phosphorus in the chain. These polyamides were made using n,n′-diphenyl methane dicarboxylic acid, m,m′-diphenyl methane dicarboxylic acid (Table 3) and n,n′-diphenyl ketocarboxylic acid.

TABLE 3. PROPERTIES OF POLYAMIDES PREPARED FROM DIPHENYLMETHANE DICARBOXYLIC ACIDS AND DIPHENYL KETODICARBOXYLIC ACID

Starting components		Softening temperature (°C)	Fibre-forming temperature (°C)
Acid	Diamine		
n,n′-$HOOCC_6H_4CH_2C_6H_4COOH$	$NH_2(CH_2)_6NH_2$	107	130–132
"	$NH_2(CH_2)_{10}NH_2$	93	98–100
m,m′-$HOOCC_6H_4CH_2C_6H_4COOH$	$NH_2(CH_2)_6NH_2$	—	83–85
"	$NH_2(CH_2)_{10}NH_2$	—	63–65
n n′-$HOOCC_6H_4COC_6H_4COOH$	$NH_2(CH_2)_6NH_2$	—	Decomposes at about 350° C

On polycondensation with diamines diphenyl ketodicarboxylic acid yields three-dimensional products thus it is impossible to compare the influence of the —CO and =P(O)R groups. Yet a comparison of the findings in Tables 1 and 3 indicates that replacement of the methylene group by a =P(O)R group in the acid radical raises considerably the softening and melting points of the polyamides. The explanation here may reside with the greater polarity of the =P(O)R group.

EXPERIMENTAL

Bis-(*n*-tolyl) methyl phosphine oxide. With vigorous stirring 142·0 g methyl phosphinic acid dichloro anhydride dissolved in 250 ml absolute ether were added dropwise to an organic magnesium compound obtained from 365·4 g *n*-bromotoluene dissolved in 250 ml absolute ether and 51·6 g magnesium. Hydrolysis with 10% H_2SO_4 yielded three phases: the bottom phase—aqueous, then a viscous, yellow oil, and the top phase—an ether solution. The aqueous phase was removed and extracted several times with ether. The ether extracts combined with oil and ether solution were washed thoroughly with 10% sodium bicarbonate solution. After the ether had been driven off a solid, yellowish mass formed that was washed thoroughly with water and recrystallized from benzene. 190·5 g *bis*-(*n*-tolyl) methyl phosphine oxide were obtained which amounted to about 73 per cent of the theoretical yield calculated on *n*-bromotoluene. The product was in the form of white crystals, melting point 143–144°C. The literature data [5] cites a melting point of 144°C.

% found: C 73·38, 73·44; H 6·88; 6·90; P 12·92, 12·46;
$C_{15}H_{17}OP$. % calculated: C 73·76; H 7·03; P 12·66

Bis-(*o*-tolyl) methyl phosphine oxide obtained in the same way as *bis*-(*n*-tolyl) methyl phosphine oxide. 182·7 g *o*-bromotoluene dissolved in 125 ml ether, 25·8 g magnesium and 71 g methyl phosphinic acid dichloro anhydride (dissolved in 200 ml ether) were reacted. After the ether had been driven off the unreacted substances were distilled off (up to 200°C). The residue was dissolved in benzene then precipitated with petroleum ether. After repeated reprecipitation from acetone the product was in the form of white crystals, melting point 120–121°C. The yield was 110 g amounting to 85 per cent of the theoretical calculated on *o*-bromotoluene.

% found: C 73·88; 73·18; H 7·00; 7·05; P 12·12; 12·27
$C_{15}H_{17}OP$. % calculated: C 73·76; H 7·03; P 12·66

Bis-(*m*-tolyl) methyl phosphine oxide, prepared in the same way as *bis*-(*n*-tolyl) methyl phosphine oxide. 135 g *m*-bromotoluene (in 100 ml ether), 19·1 g magnesium and 52·5 g methyl phosphinic dichloro anhydride (in 100 ml ether) were reacted. The yield of *bis*-(*m*-tolyl) methyl phosphine oxide was 60·8 g, or 64 per cent of the theoretical. When recrystallized from methyl alcohol this product had a melting point of 78°C and consisted of white crystals soluble in benzene, ethyl and methyl alcohols.

% found: C 74·13; 74·26; H 7·06; 7·12; P 12·76; 12·92.
$C_{15}H_{17}OF$. % calculated: C 73·76; H 7·03; P 12·66

Bis-(*n*-carboxyphenyl) methyl phosphine oxide was prepared by oxidation of *bis*-(*n*-tolyl) methyl phosphine oxide by potassium permanganate in an aqueous piridine medium by the technique reported by Morgan and Herr [5]. 186·3 g *bis*-

(*n*-tolyl) methyl phosphine oxide, 877 g potassium permanganate and 950 ml piridine were reacted and the resulting acid melted at 285–287°C. The yield was 156·7 g, or 68 per cent of the theorectical. The analysis results are given in Table 4.

Bis-(*m*-carboxyphenyl) methyl phosphine oxide was prepared by the method reported by Morgan and Herr [5]. 63·6 g *bis*-(*m*-tolyl) methyl phosphine oxide, 300 g potassium permanganate and 320 ml piridine were reacted, followed by acidification of the mixture with HCl, whereupon a white oil precipitated out which solidified on boiling with water. This was then recrystallized from methyl alcohol. The yield was 21·6 g (25 per cent of the theoretical), melting point 282–283°C. The analysis results are listed in Table 4. The acid was soluble in methyl and ethyl alcohols but not in sulphuric or petroleum ether and acetone.

TABLE 4. PROPERTIES OF PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS

Formula	Melting point (°C)	Acid number mg KOH		Analysis (%)					
				C		H		P	
		Found	calculated	Found	Calculated	Found	Calculated	Found	Calculated
$C_6H_5P(O)n\text{-}C_6H_4COOH)_2$	340–342	294	306	65·22	65·49	4·26	4·11	8·37	8·45
				66·0		4·38		8·04	
$CH_3P(O)(n\text{-}C_6H_4COOH)_2$	285–287	336	368	58·5	59·20	4·94	4·31	9·92	0·15
				59·31		4·70		10.09	
$CH_3P(O)(m\text{-}C_6H_4COOH)_2$	282–283	332	368	59·13	59·20	4·51	4·31	10·20	10·15
				59·45		4·31		10·17	
$CH_3P(O)\,(o\text{-}C_6H_4CO)_2O$	163–164	372	392	63·04	62·95	4·09	3·87	10·79	10·82
				62·88		3·97		10·73	

The anhydride of *bis*-(*o*-carboxyphenyl) methyl phosphine oxide was obtained by oxidation of *bis*-(*o*-tolyl) methyl phosphine oxide in a similar manner to the foregoing. 71 g *bis*-(*o*-tolyl) methyl phosphine oxide, 335 g potassium permanganate and 350 ml piridine were reacted. After recrystallization from methanol 17·1 g of the anhydride were obtained (yield 20 per cent of the theoretical), melting point 163–164°C. The analysis results are shown in Table 4.

Preparation of the salts. With gentle heating 0·095 mol acid and 0·099 mol diamine (excess 5 per cent) were dissolved in 15 ml ethyl alcohol. The slightly yellow, viscous solution formed was filtered, thoroughly washed with benzene, the bottom phase removed and desiccated *in vacuo* at 50°C. The salts were readily soluble in water, methyl and ethyl alcohols but insoluble in sulphuric and petroleum ethers, acetone and benzene. The melting points and analysis results are reported in Table 5.

TABLE 5. SALTS OF ALIPHATIC DIAMINES WITH PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS

Salts	Melting point (°C)	Analysis (%)							
		Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
Salts of *bis*-(*n*-carboxyphenyl) phenyl phosphine oxide with diamines									
		59·41		6·33		5·99		7·05	
Tetramethylene diamines	293–240	59·59	61·02	6·24	6·18	6·31	6·55	7·28	5·97
Hexamethylene diamines	212–214	61·76	62·38	6·93		5·65		5·76	
		62·19		6·92	6·64	5·71	6·11	5·61	5·59
Octamethylene diamine	238–240	65·03	65·88	6·91		6·04		5·82	
		65·76		6·89	6·91	6·26	6·06	6·02	5·48
Nonamethylene diamines	201–204	64·93	64·19	7·17		5·58		5·01	
		65·19		7·27	7·25	5·63	5·71	4·95	5·16
Decamethylene diamines	216–218	64·12	64·73	7·48	7·42	5·33		5·54	
		64·02		7·26		5·60	5·56	5·50	5·03
Salts of *bis*-(*n*-carboxyphenyl)-methylphosphine oxide with diamines									
Tetramethylene diamines	252–253	54·69	55·60	6·64	6·63	7·33	7·52	7·11	6·83
		54·49		6·50		7·11		7·06	
Hexamethylene diamines	284–285	58·63	59·98	6·79	6·95	7·13	7·36	7·31	6·67
		58·89		6·83		7·33		7·47	
Octamethylene diamine	199–201	58·82	59·20	7·08	7·56	6·25	6·64	5·75	6·60
		58·87		7·49		6·15		5·69	
Nonamethylene diamines	210–212	60·91	60·00	7·54	7·76	5·90		5·58	
		60·72		7·53		5·82	6·44	5·51	5.67
Decamethylene diamines	236–238	61·07	60·71	7·59	7·94	6·60	6·26	6·21	5·67
		61·29		7·87		6·25		6·00	
Salts of *bis*-(*n*-carboxyphenyl) methylphosphine oxide with diamines									
Hexamethylene diamines	150–152	57·11		7·29		6·33		6·01	
		57·28	57·62	7·11	7·14	6·53	7·08	6·18	—
Octamethylene diamines	139–141	60·40		7·70		6·92		5·37	
		60·45	59·20	7·88	7·56	6·74	6·64	5·05	—
Nonamethylene diamines	135–138	61·03		7·69		6·21		5·60	
		60·95	6·60	7·84	7·76	6·08	6·44	5·65	5·83
Decamethylene diamines	144–146	61·30		8·09		6·38		5·58	
		61·55	60·71	8·09	7·95	6·18	6·27	5·47	5·67

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CONCLUSIONS

(1) Polyamides are prepared from phosphorus-containing dicarboxylic acids and a series of aliphatic and aromatic diamines.

(2) The polyamides synthesized from aromatic diamines are distinguished by a far higher melting point than those from aliphatic diamines. This is associated with the effect of even chains in the aliphatic series of diamines and with the isomerism in the distribution of the functional groups in the aromatic series of diamines.

(3) The softening point and fibre-forming temperature of the polyamides based on acids with a phenyl substituent on the phosphorus atom are higher than the corresponding ones of the polyamides with a methyl substituent.

(4) The powerful interaction between the chains in the polyamides which becomes apparent in the high melting point occurs with the n-configuration of the functional groups in all the examined phosphorus-containing acids.

(5) Replacement of the CH_2 group on the $=P(O)R$ group in an acid produces a considerable rise in the melting point of the polyamides attributable to the higher polarity of the $=P(O)R$ groups.

Translated by R. S. A. CAMERON

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STUDIES IN THE FIELD OF MECHANOCHEMISTRY — VI. A STUDY OF THE DISINTEGRATION OF POLYSTYRENE IN SOLUTIONS UNDER THE INFLUENCE OF ULTRASONIC VIBRATIONS*

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(*Received* 2 *February* 1959)

A SUBSTANTIAL number of studies on the disintegration of polymers by ultrasonic vibrations are reported in the literature. Nonetheless it is extremely difficult to infer any general conclusions as to the mechanism and kinetics underlying the mechanochemistry associated with the changes which come about in high molecular compounds under the influence of ultrasonic vibrations, because the majority of the workers make no allowance for the power of ultrasonic vibrations under water and fail to pay sufficient attention to such important factors as the extent to which the energy of the vibrations is used up, the frequency of the vibrations, the concentration of the solution, the presence of acceptor radicals, etc. Furthermore, until recently the character of the processes that come into play when high intensity ultrasonic vibrations act on polymer solutions had not been studied. At the same time a study of disintegrating—combining processes occurring on exposure of polymer solutions over a wide range of ultrasonic vibration intensities would make it possible: (1) to deduce general characterizing criteria for the kinetics of ultrasonic disintegration, (2) to determine the mechanism of these processes, and (3) to evolve more rational methods of using ultrasonic vibrations for mechanochemical block-graft copolymerization.

Although the attempts of a number of authors [1–3] to approach the ultrasonic disintegration of polymers in terms of formal kinetics led to a specific mathematical interpretation, they threw no light on the mechanism underlying the process. The diversity of the factors that operate in the ultrasonic vibration disintegration of polymers in solution prompts the need to find a method of characterizing the process using constants of a more general nature which are not governed by the particular conditions under which the process is conducted.

One of the key factors of the mechanochemical process is the energy yield (α), indicating the number of mols of product formed per unit of energy supplied.

* Vysokomol. soedin. 1: No. 5, 688–696, 1959.

The determination of α gives an immediate idea of the number of molecules activated by the quantity of mechanical energy that has entered the system. By experiment $\alpha = K/U$, where $U = IS$, K = reaction rate constant, I = intensity of ultrasonic vibration, S = area of vessel bottom. Consequently to determine the kinetics of ultrasonic disintegration, the relationship of K to the energy supplied per unit weight of the polymers in solution needs to be determined.

The differential equation for the disintegration inferred from a simplified formula [4] can be written in the form:

$$\frac{dN_{x_t}}{dt} = -K(x-1),$$

where N_{x_t} = number of macromolecules with a chain of x units long, and K = disintegration rate constant independent of the chain length for chains exceeding a critical size (y for the given conditions) and equal to zero for chains smaller than y.

The solution $N_{x_t} = N_{x_0} e^{-K(x-1)t}$, where N_{x_0} = number of chains of length x_0 at $t = 0$ is found from the equation $N_{x_0} = N_0 p^{x-1}(1-p)^2$, where the probability factor $p = P/P+1$ (N_0 = normal number of monomer units for a polymer with a mean degree of polymerization P). Let $K = f(U)$. Assume that the reaction constant has to be linearly proportional to the acoustic energy U, viz. $K = xU$: here the disintegration may be described by the equation:

$$N_{x_t} = N_{x_0} \exp\{-(allt/vc)(x^{-1})\}$$

where v = volume of exposed specimen, c = concentration of solution. The kinetic curves are then functions of the relation $Ut/vc = q$. It would here be convenient for establishing the effect of the acoustic energy on the kinetics of ultrasonic disintegration to take as criteria $Ut/vc = q$ (or the "q factor").

It will be apparent from a study of the relationship of the disintegration rate constant to q that the "mechanical activation energy" can also be calculated. If, on the assumption that K is linearly proportional to q, the concentration is proportional to the increase in power, the energetic yields can be expected to remain constant. The q-factor enables a comparative determination to be carried out of the results obtained by the various authors who studied the ultrasonic disintegration of these or other polymers in solutions of differing concentration throughout a wide acoustic energy range.

The present work reviews the experimental results found by the authors when studying the ultrasonic disintegration of polystyrenes over a wide range of frequencies and acoustic energies. Examination of the change in $[\eta]P$, xK and of the increase in the number of microradicals as a function of the q-factor enabled a number of theoretical generalizations to be inferred and made possible a more complete evaluation of the kinetics underlying the mechanochemical processes that occur under the action of high intensity ultrasonic vibrations on solutions of polymers.

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EXPERIMENTAL

Generators UAG-30, UAG-60 and UAG-100 of a design worked out at the anisotropic structures laboratory of the Academy of Sciences of the USSR [5] and with an output power of 30, 60 and 100 kW respectively were used in our experiments. The vibration sources were ultrasonic "guns" with a special fixing for the piezoquartz emitter plate with silvering of 38 mm diameter. The transmitting medium was transformer oil. The ultrasonic vibrations from the quartz and the reflector plate passed through semi-corrugated glass covering the outlet from the gun into the upper water-filled reservoir. The reaction vessel (Fig. 1) was of cylindrical shape, 32 mm diameter and 150 mm long fitted with a stopper or ground glass assembly to admit argon. The thick base of the vessel was of semi-corrugated glass. The vessel was mounted in the upper reservoir by means of an adjusting ring strictly parallel to the surface of the quartz (Fig. 2). The apparatus used operated at frequencies of 350 and 750 kc/s and of 1·0, 1·5 and 2·0 Mc/s in both continuous and discontinuous operation.

The ranges of the experimentally attainable ultrasonic vibration intensities determined calorimetrically were 5–50 W/cm² (50 W/cm² with pulsed vibrations) at a frequency of 350 kc/s and from 5–400 W/cm² (200–400 W/cm² with pulsed vibrations) at a frequency of 1·5 Mc/s. At other frequencies the intensity was of the same order thus as the frequency rose a higher limit intensity was reached in the 50–400 W/cm² range. The exposures were timed in seconds by an electrical device to an accuracy of $\pm 0{\cdot}005$ sec.

The experiments involving low intensity ultrasonic vibrations were accomplished with a generator designed as a Hartley oscillator in combination with a piezoquartz source using frequencies of 300 kc/s and 1·2 Mc/s. In view of the large amount of heat developed on exposure of the solutions to high intensity ultrasonic vibrations the exposure times were restricted to from 0·5 to 10 sec followed by cooling of the system for 3 min with ice. By this means the change in temperature that attended exposure was minimized. 20 ml solutions were exposed simultaneously. The test specimens were polystyrenes of three molecular weights, i.e. 153,000, 220,000 and 823,000, which had been purified by three-fold reprecipitation into methanol from a 1% solution in benzene. The reprecipitated polystyrene was desiccated at 60°C and then *in vacuo*. The solutions prepared for the tests consisted of 0·1–1·0 g of polystyrene in 100 ml of cryoscopic benzene washed with H_2SO_4 and distilled over metallic sodium. Iodine, which was used as the radical acceptor, was purified by sublimation. Whilst the experiments were being conducted in an oxygen-free atmosphere argon (and in some cases nitrogen) was passed into the reaction vessel for 1½ hr after first being freed from oxygen in a system comprising two columns containing a solution of an ammonium complex of cuprous chloride, one column with pyrogallic acid, two columns with H_2SO_4 of different concentrations and one column with glass wool. The gas released in the second column did not give

the reaction for oxygen. The results of the ultrasonic disintegration were assessed from the viscometric findings. To calculate the characteristic viscosity we used the formula [6] $[\eta]=3(\eta_{rel}^{1/3}-1)/c$. η_{rel} was measured for 1% solutions of polystyrene in benzene at $20°\pm0{\cdot}05°C$. The values of $[\eta]$ found from this formula are slightly larger than the same values derived by extrapolating η_{sp}/c at $c=0$ in the coordinates η_{sp}/c and c. Nevertheless this formula gives satis-

FIG. 1. Reaction vessel.

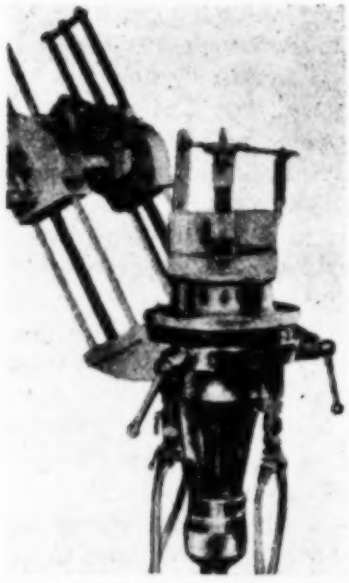


FIG. 2. Mounting of vessel on source.

factorily comparable results for the examined specimens of polystyrene. The degree of polymerization at intermediate viscosity was found from the formula $P=773[\eta]$ derived from the equation $P=8\times10^3\times[\eta]$ for the case of determining $[\eta]$ at 20°C [7].

The number of ruptured bonds and the number of radicals formed besides were calculated from the findings relating to viscosity and to the degree of polymerization at intermediate viscosity. The relationship between the number of ruptured bonds (mol/l.) and the degree of polymerization prior to disintegration P_0 and after disintegration P is given by the formula [8]

$$x=c\left(\frac{1}{P}-\frac{1}{P_0}\right),$$

where c = concentration of solution in base mols/l. If we assume that a single rupture in a macromolecule will produce two radicals we shall obtain for the

number of radicals formed $R=2x$, or expressed in terms of viscosity and concentration in g/100 ml, $x=1{\cdot}245\times10^{-5}\,\Delta(\eta^{-1})$ and $R=2{\cdot}49\times10^{-5}\,\Delta(\eta^{-1})$.

Having determined the change in the degree of polymerization of the polystyrene under the assumed conditions as a function of the period of exposure, we can work out the disintegration rate constant K_{di}, using the formula [4]:

$$K_{di}=\frac{2}{P_0 t}\left(\frac{P_0}{P_t}-1\right)$$

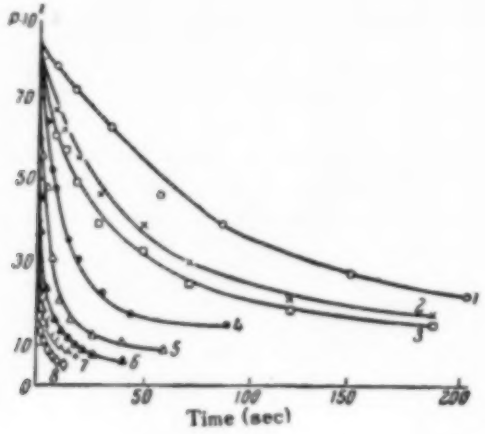
The table illustrates the ultrasonic disintegration of polystyrene ($P_0=8200$) in benzene solutions ($c=0{\cdot}10$ g/100 ml) for a vibration intensity of 50 W/cm², $v=1{\cdot}5$ Mc/s, on exposure to an intermittent beam for 2 sec followed by 3 min cooling.

TABLE 1. BASIC PARAMETERS AS A FUNCTION OF THE EXPOSURE TIME OF A POLYSTYRENE SOLUTION (c = 0·10 g/100 ml); ULTRASONIC VIBRATIONS I = 50 W/cm² and V = 1·5 Mc/s

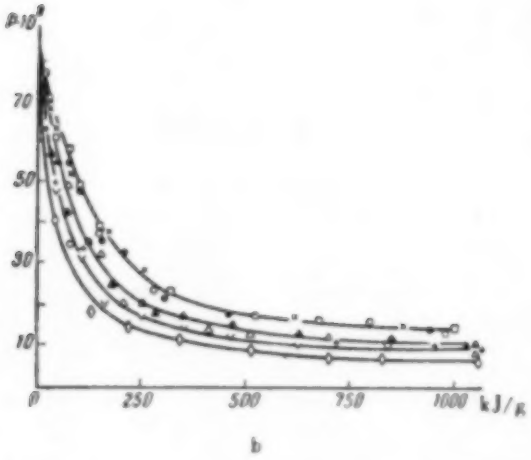
Total exposure (sec. t)	Energy consumption (J ItS)	Volumetric energy density J/cm³ $\frac{ItS}{v}$	Specific energy KJ/g $\frac{ItS}{vs}=q$	Relative viscosity η_{rel}	Intrinsic viscosity according to Sakurade [6] $[\eta]$	Mean degree of polymerization (P)	Reciprocal of decrease in viscosity $\Delta[\eta^{-1}]$	No. of ruptured bonds mol/l. $\times 10^6$	No. of radicals formed mol/l·R $\times 10^6$	Disintegration rate constant $K_i \times 10^5$
2·00	700·0	35·00	35·00	1·538	7·20	5570	44·6	0·555	1·11	5·73
4·22	1417·0	73·50	73·50	1·508	6·27	4850	66·7	0·830	1·66	4·00
8·33	2912·0	145·60	145·60	1·276	3·87	2990	164·1	2·041	4·082	5·11
12·15	3249·0	212·80	212·80	1·174	2·52	1950	302·5	3·763	7·526	6·43
16·05	5614·0	280·70	280·70	1·145	2·10	1625	381·9	4·76	9·52	6·15
24·04	8414·0	420·70	420·70	1·118	1·71	1320	490·5	6·10	12·20	5·29
30·00	10500·0	525·0	525·0	1·105	1·53	1180	559·3	6·96	13·92	4·84
40·22	14077·0	703·5	703·5	1·092	1·35	1040	646·4	8·05	16·10	4·20
60·00	21000·0	1050·0	1050·0	1·084	1·21	935	732·0	9·11	18·22	3·17

Fig. 3a plots findings relating to the ultrasonic disintegration of polystyrene in benzene, $c=0{\cdot}10$ g/100 ml with $P_0=8200$ calculated, as indicated above, in terms of the intensity at 1·5 Mc/s for various periods of exposure. The curves were traced at I = 5 W/cm², 10 and 15 W/cm² with 10 sec exposure to an intermittent beam followed by 3 min cooling; at I = 30·50 and 100 W/cm² with 2 sec exposure to an intermittent beam followed by 3 min cooling; at I = 150 W/cm² with 4 sec exposure to an intermittent-pulsed beam followed by 3 min cooling and at a t/t' ratio of 1/4; at I = 250 W/cm² with 2 sec exposure to an intermittent-pulsed beam followed by 3 min cooling for the same t/t' ratio, and at I = 390

W/cm² with 1 sec exposure to an intermittent-pulsed beam followed by 3 min cooling at the same t/t' ratio where the duration of the pulse t was 400 μsec and the pause 1200 μsec.



a



b

FIG. 3. Mean degree of polymerization at different intensities W/cm² as a function: (a) of the exposure time; (b) of the q-factor (a) 1—5, 2—10, 3—15, 4—30, 5—50, 6—100, 7—150 (intermittent and intermittent-pulsed beam); 8—250 (pulsed beam); (b) ○—5; ×—10; □—15; ●—30; ▲—50; △—100; +—150; ▽—150 (pulsed beam); ◇—250 (pulsed beam).

As follows from the Table and from Fig. 3a the values of the intrinsic viscosity and degree of polymerization decrease and the numbers both of the ruptured bonds and also of the radicals formed thereafter increase with increasing ex-

posure, energy expenditure, energy density and degree of polymerization. The disintegration rate constant K_{di} remains steady to within one order of magnitude but tends to decrease with increasing exposure. In its general character each of the curves in Fig. 3a is analogous to those previously obtained by various authors [2, 3, 9] independently at different (lower) intensities and different frequencies with this difference, i.e. in the present case the entire process was accomplished in the space of seconds and tenths of seconds as against the hours and tenths of hours taken earlier. As the intensity grows the curves fan out and approach the ordinate axis, thus attesting an acceleration of the ultrasonic disintegration process.

Fig. 3b plots the degree of polymerization of the same polystyrene specimens in benzene solution as a function of a more general parameter than time, i.e. the q-factor. Throughout the range of intensities from 5 to 30 W/cm² the experimental points lie satisfactorily on a single curve which implies that for equal energy expenditure throughout this range the same disintegration is produced. As the intensity rises further to 250 W/cm² the curves diverge but on completion of disintegration they converge to a common lower limit indicating a more complex character of the relationship between the mean degree of polymerization P and the q-factor in this range of intensities.

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Fig. 4a and b plot the mean number of ruptured bonds as a function of the exposure time for a range of intensities. Both graphs follow a common pattern: the curves fan out with rising intensity whilst tending towards the ordinate axis besides which in the final stages of disintegration the order of the concentration changes from 10^{-6} to 10^{-5} base mol/l. Fig. 4c plots the number of ruptured bonds as a function of the q-factor at different intensities. The experimental intensity values 5, 10, 15 and 30 W/cm² are grouped about a single, common curve.

When the intensity changes to 50 and 100 W/cm² more bonds are ruptured with increasing q. The values for 250 W/cm² are grouped about the curve for 100 W/cm² and those for 150 W/cm² lie on a lower curve.

Fig. 5 gives the logarithm of the disintegration rate constant as a function of the reciprocal of the power. The proportionality between lg K' and $1/U$ was not, as anticipated, linear throughout the extensive range of intensities studied, but far more complex. However, for narrow power ranges, e.g. 5 to 30 W/cm² the proportionality is found in a first approximation to be linear.

Fig. 6 shows a plot of the threshold values of the energy consumption against power. It follows from the graph that the energy consumption rises with the power supplied and attains values of the order of 10^{-8}–10^{-7} mol/kcal.

Fig. 7a gives as a function of the q-factor the results obtained in experiments on disintegration of polystyrene with $M_0 = 223{,}000$ in benzene solutions with concentrations of 0·10, 0·50 and 100 g/100 ml under the action of ultrasonic vibrations with a frequency of 300 kc/s and an intensity of 0·5 W/cm². The intrinsic viscosity values as a function of q lie satisfactorily on a common curve

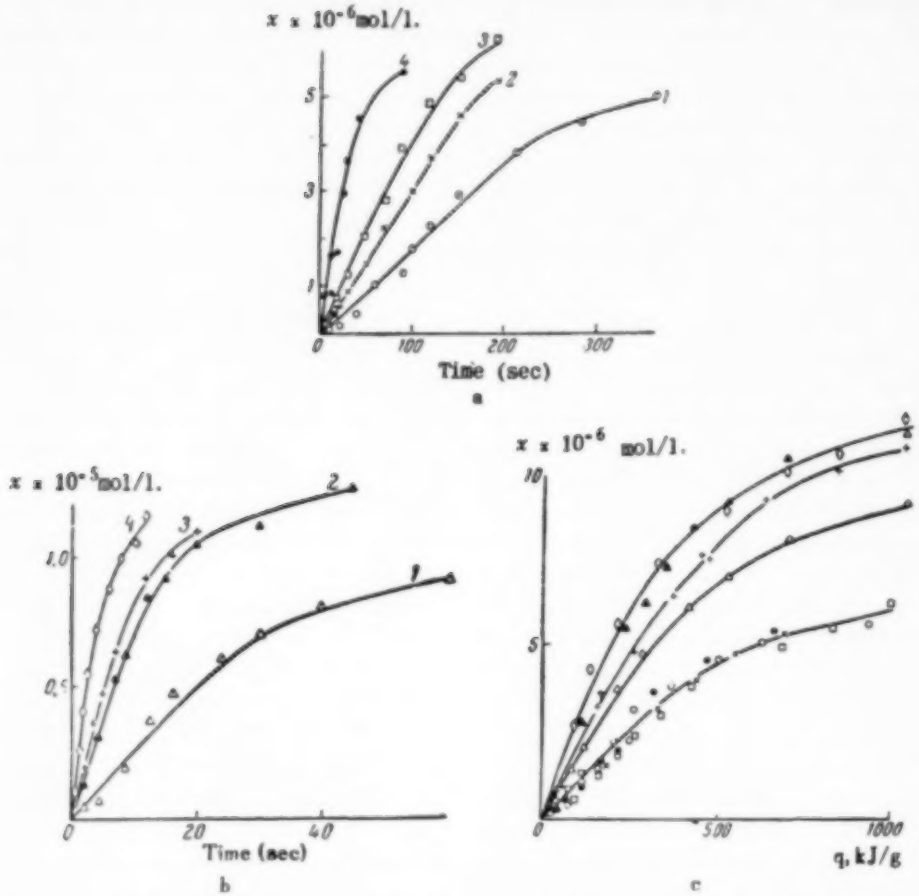

FIG. 4. Mean number of ruptured bonds at various intensities (W/cm²) as a function: (a, b) of the exposure time: (c) of the q-factor. (a) 1—5, 2—10, 3—15, 4—30; (b) 1—50, 2—100, 3—150, 4—250; (c) ○—5, ×—10, □—15, ●—30, △—50, +—100, ▲—150, ◇—250.

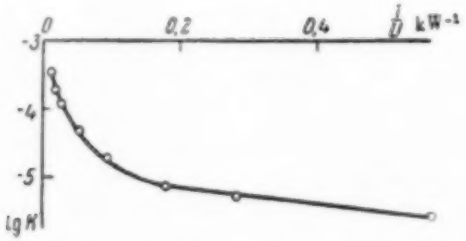

FIG. 5. Plot of lg K versus 1/U.

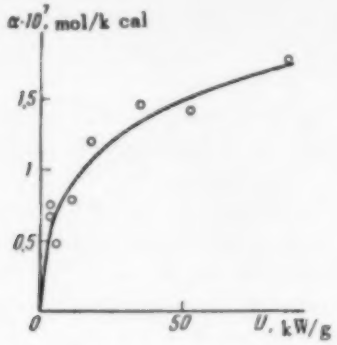

FIG. 6. Threshold energy consumption α as a function of the power supplied.

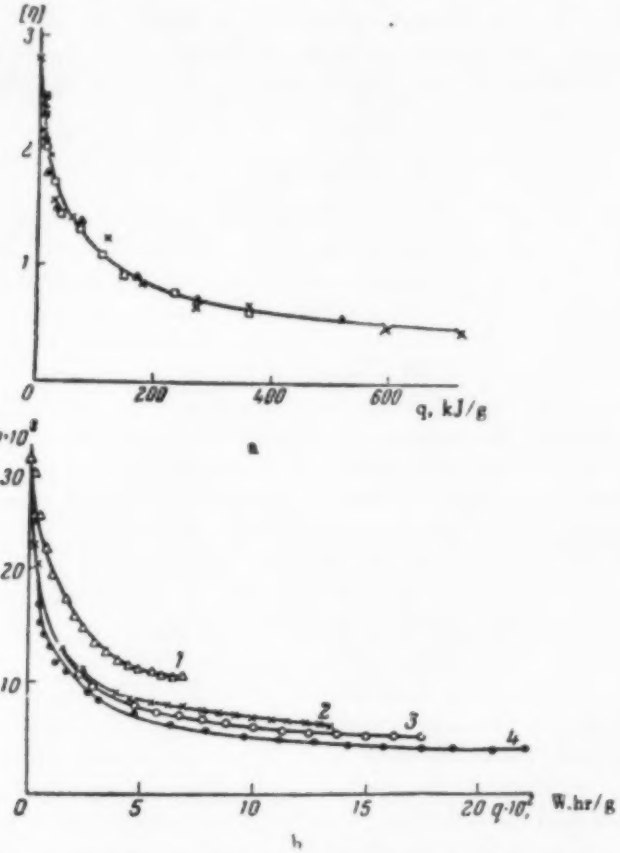

FIG. 7. Mean degree of polymerization at a series of concentrations (g/100 ml) as a function of: (a) the q-factor (b) of q according to Mostafa [4] (W/cm²) at different intensities. (a) ▲ — 0·10, × — 0·5, □ — 1·0; (b) 1 — 4·98, 2 — 9·58, 3 — 12·56, 4 — 15·80.

for all three concentrations. Plots of the number of ruptured bonds against q for the same concentrations of polystyrene in benzene solutions exhibit an analogous trend.

By way of an example to illustrate the practicability of the present method Fig. 7b plots the mean degree of polymerization against the q-factor evaluated in accordance with the findings derived by Mostafa [4] for the ultrasonic disintegration of a solution of polystyrene with $P=3600$ in benzene (1·0 g/100 ml) at a frequency of 750 kc/s and with intensities of 4·98, 9·58, 12·50 and 15·80 W/cm². Unfortunately the author did not give the dimensions of the radiating quartz surface nor the diameter of the reaction vessel, hence the calculated values are relative. The general trend of the curves is analogous to that of the ones above based on our experiments although different P values are obtained in the examined range for equal values of q.

The curve for $I=4·98$ W/cm² lags behind the three remaining curves which lie close together. The mean degrees of polymerization at intensities of 9·58, 12·50 and 15·80 W/cm² have a slight tendency to fall off in ascending order at the same q-factor values.

DISCUSSION

Analysis of the results obtained reveals the q-factor to be a more general parameter of the ultrasonic disintegration of polymers than the exposure. The use in the present paper of high intensity ultrasonic vibrations up to 250, and in some cases up to 390 W/cm², resulted in a considerable acceleration in the disintegration rate compared with those cited in the literature. Thus, for instance, the overall rate constant for an intensity of 250 W/cm² is $3·60\times10^{-4}$ sec^{-1} and the exposures (cf. Fig. 3a and b) are expressed in seconds and tenths of seconds, greatly complicating comparison and analysis of the results obtained. Comparison of the values for the mean degree of polymerization in terms of the q-factor leads to the conclusion that the disintegration is not a function of the intensity and the exposure individually, but of their product, i.e. the energy consumed. Bearing this in mind it is possible to examine separately both the influence of the intensity and the influence of the exposure. Fig. 4a shows that although the increase in intensity from 5 to 30 W/cm² entails an increase in the rate of the process (cf. Fig. 3a) it still gives the same result in terms of q. A further rise in intensity to 250 W/cm² also accelerates the rate of disintegration (cf. Fig. 3a) but, in contrast with the lower intensity range, it also produces a slight falling-off in the mean degree of polymerization. In this respect it is interesting to compare the cited results with the results in paper [4] relating to the disintegration of a solution of polystyrene ($P=3260$) in benzene at a concentration of 1·0 g/100 ml and a frequency of 750 kc/s (cf. Fig. 7a). With increasing intensity in the range from 5 to 16 W/cm² under these conditions a slight diminution in the mean degree of polymerization takes place as a function of q. We consider that a similar falling-off in the mean polymerization rate as a function of q with increas-

ing intensity can be accounted for by a change in the energy supply conditions associated with the reaction. With increasing intensity the spatial energy distribution becomes less uniform and this in turn brings about a rise in the concentration of molecules in a state of excitation. Assuming the rate of de-activation to remain constant, inasmuch as it is not directly associated with the acoustic phenomena in the system, a non-linear increase in the disintegration rate constant K with the intensity is possible. An analogous relationship is valid between the number of ruptured bonds and q .Over a given narrow range of intensities this number does not depend upon the intensity in terms of q but increases with the intensity for equal consumptions of energy. Thus the anticipated linear proportionality between lg K and $1/U$, although it applies in first approximation in a narrow intensity range, is not valid throughout the whole of the extensive range of powers studied (Fig. 5). The increase α in the consumption of energy, calculated from the q-factor as a function of the intensity (Fig. 6), may serve to illustrate the likelihood of a change in the activation rate of the process. Calculation of the maximum activation energy on the basis of α and q for a series of experiments at 250 W/cm² assuming that only that part of the energy is used which impinged on the ruptured bonds, gave a value $E \approx 40{\cdot}0$ kcal/mol. From this value it is impossible to work out the activation energy proper but by using it as a basis it is possible to demonstrate that the energy consumption coefficient must increase with a rise in intensity if $E = \text{const}$.

To illustrate the nature of the relationship between the disintegration findings and q details are given of the influence of concentration (Fig. 7a) on the quantity $[\eta]$. It is shown that the mean degree of polymerization in the present case depends upon q and for equal values of q is independent of the concentration. Thus any conclusions as to the influence of the concentration on the extent of the disintegration ought to take into account q and not, as previously, the exposure alone [11]. Precisely the same conclusion regarding the ultimate degree of polymerization as a function of the intensity should be drawn for equal values of q and not, as in the case mentioned earlier [4], for equal values of t.

CONCLUSIONS

(1) The disintegration kinetics are studied of three polystyrene specimens with different mean molecular weights under the action of ultrasonic vibrations of intensity from 5 to 400 W/cm².

(2) A more general disintegration parameter than time is derived—the q-factor—and the quantity "threshold energy consumption" α.

(3) The formal kinetic mechanisms as a function of the exposure and the q-factor are indicated for the disintegration of polystyrene under the action of ultrasonic vibrations. The rate constants and threshold energy consumptions α are calculated.

(4) The relationship of K_{di} and α to the intensity of the ultrasonic vibrations are found.

Translated by G. CAMERON

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GEOMETRY OF LINEAR POLYMERS—VI. THE THEORY OF VOLUME EFFECTS IN POLYMER CHAINS*

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(*Received* 19 *March* 1959)

1. INTRODUCTION

THE properties of macromolecules in solution are conditioned both by the structure and the elasticity of the chain and also by the interactions between the chain segments and the molecules of the solvent. These interactions decrease extremely rapidly with distance and may therefore be described as a means of interpolating the effective excluded volume as in the theory of real gases [1]. Hence the interactions of a remote order have been termed "volume effects".

The approximate thermodynamic theory proposed by Flory [2–5] pertaining to the influence of the volume effects on the dimensions of macromolecules in solution leads to the following expression for the coefficient $\alpha=(\bar{h}^2/\bar{h}_0^2)^{1/2}$ ($\bar{h}^2=$ mean square distance between the ends of the macromolecules in solution, and $\bar{h}_0^2=$the value of $\bar{h}^2$ in the absence of volume effects);

$$\alpha^5-\alpha^3=2C_M\psi_1\left(1-\frac{\theta}{T}\right)M^{1/2}. \tag{1}$$

Here $\psi_1=$a parameter characterizing the entropy associated with the mixture composed of polymer chain segments and solvent molecules, $\theta=$characteristic temperature (for the given polymer-solvent pair), $M=$molecular weight of polymer,

$$C_M=\frac{2z}{2^{5/2}\pi^{3/2}}\frac{\bar{v}^2}{N_A v_1}\left(\frac{M}{\bar{h}_0^2}\right)^{3/2} \tag{2}$$

$\bar{v}=$partial specific volume of polymer, $N_A=$Avogadro's number, $V_1=$molar volume of solvent. At $T=\theta\alpha=1$, viz. volume effects are absent.

Further, in a series of papers [6–11] where the space effects were dealt with by a strict statistical method (valid for small volume effects), the following result is obtained:†

$$\alpha^2=1+\frac{4z}{3}+\ldots. \tag{3}$$

* Vysokomol. soedin. **1**: No. 5, 715–729, 1959.

† In paper [11] the following term of the series expansion of α^2 over z is also derived.

where

$$z=\left(\frac{3}{2\pi}\right)^{3/2}\frac{\sqrt{N}\cdot v_0}{a^3} \tag{4}$$

(N=number of chain segments, V_0=effective excluded volume of a segment, a=effective length of a segment). The relationship between V_0 and the thermodynamic parameters of the polymer-solvent system may be established from a comparison of the expressions for the second virial coefficient close to the θ-point derived by thermodynamic [12], [5] and statistical [13] methods (these expressions in the vicinity of the θ-point are independent of the chain model used). We have (cf. [14])

$$v_0=2\frac{V_s^2}{V_1}\psi_1\left(1-\frac{\theta}{T}\right), \tag{5}$$

where V_s and V_1=respectively the volumes of the polymer chain segments and of the solvent molecule. Thus, using $NV_s=M\vartheta/N_A$, we find

$$z=\frac{4}{3\sqrt{3}}C_M\psi_1\left(1-\frac{\theta}{T}\right)\sqrt{M}. \tag{6}$$

By means of equation (6) Flory's equation can be expressed by the parameter z (cf. [15]):

$$\alpha^5-\alpha^3=\frac{3\sqrt{3}}{2}z. \tag{7}$$

The series expansion of (7) over z will give:

$$\alpha^2=1+\frac{3\sqrt{3}}{2}z, \tag{8}$$

viz. the coefficient at z is greater by a factor of about 2 than in the exact equation (3).

The discrepancy between the strict and the approximate theories is attributable essentially to two causes. Firstly the approximate theory makes no allowance for the bonding of the segments into a chain since it considers not the real chain but the segments of Gaussian distribution with respect to the centre of gravity. Secondly Flory's theory fails to take into account that the volume effects lead to a non-Gaussian distribution function $W(h)$ for the end-to-end distance. The latter has been taken into consideration by Vol'kenshtein and the author of the present paper [15, 16] who both obtained an approximate expression for $W(h)$.

The non-Gaussian character of the function $W(h)$, which is determined by the occurrence of the volume effects, implies that the influence of the volume effects on the chain dimensions cannot be considered as a simple increase in the length of a statistical element of the chain. It follows from this in particular that, generally speaking, the volume effects act differently on the various geometrical chain characteristics that have the dimension of length. Allowance for this effect which may be described as the heterogeneous swelling of a sphere in the light scat-

tering [17, 18] and hydrodynamic properties [19, 20] theories of macromolecules in solution, has led to considerably improved agreement between these theories with experiment.

The aim of the present paper is to obtain an accurate expression for $W(h)$ in terms of the strict statistical theory of volume effects and to review certain consequences of the non-Gaussian character of this function. The accurate expression for $W(h)$ is compared with the approximate expression derived previously [15, 16] and consideration is given to the way in which Flory's theory alters by making an approximate allowance for the non-Gaussian character of the distribution function and for the anisotropic swelling of the sphere.

2. METHOD OF CALCULATION AND RESULTS FOR THE MEAN CHAIN DIMENSIONS

Basically the method employed by us to calculate the function $W(h)$ was analogous to that proposed by Fixman [11] (cf. also [21, 22]). Nevertheless we shall quote here the main intermediate results of the calculations because they are essential for a series of applications of this method [20].

We shall consider what is called the "pearl necklace model" of the polymer chain consisting of $N+1$ segments (numbered from O to N) freely linked by N immaterial bonds of length a. The distribution function for the coordinates of the p^{th} and t^{th} chain segments have the form:

$$f(p,t)=\int\cdots\int f\{k\}\frac{d\{k\}}{d(p)\,d(t)}=\int\cdots\int f^0\{k\}e^{-\frac{V\{k\}}{RT}}\frac{d\{k\}}{d(p)\,d(t)}\,. \tag{9}$$

where $f\{k\}$=the complete distribution function for the set of coordinates $\{k\}$ of all the chain segments, (p)=set of coordinates of the p^{th} segment, $f^0\{k\}$ =distribution function in the absence of interaction between the chain segments, and $V\{k\}$=interaction energy of all the chain segments. Taking into account only the pairs of interactions, we obtain $V\{k\}=\sum_{i<j}u(\vec{r}_{ij})$, where $u(\vec{r}_{ij})$ = interaction energy of the segments i and j. Since $u(\vec{r}_{ij})$ quickly decreases with increasing distance $r_{ij}=|\vec{r}_{ij}|$, the function $\varphi(\vec{r}_{ij})=1-\exp[-u(\vec{r}_{ij})/RT]$, can readily be interpolated which differs appreciably from zero only at low values of r_{ij}. Then

$$e^{-\frac{V\{k\}}{RT}}=\prod_{i<j}[1-\varphi(\vec{r}_{ij})]=1-\sum_{i<j}(\varphi(\vec{r}_{ij})+\ldots \tag{10}$$

On the right-hand side of equation (10) each term participating in the double sum (over i and j) corresponds to the "collision" of two chain segments, and the following terms simultaneously correspond to the collision of two pairs of segments and so on. If the volume effects are small, i.e. the probability of collisions is slight, the following terms may be disregarded, thus

$$f(p, t)=f^{\circ}(p, t)-\sum_{i<j}\int\int f^{\circ}(p, t, i, j)\,\varphi(\vec{r}_{ij})\,d(i)\,d(j)\,, \tag{11}$$

where

$$j(p, t, i, j)=\int\ldots\int f\{k\}\,\frac{d\{k\}}{d(p)\,d(t)\,d(i)\,d(j)}$$

=distribution function for the coordinates of the four chain segments. Since integration over $\vec{r}_{ij}$ in fact reduces to integration over a small zone close to zero (outside this zone $\varphi(\vec{r}_{ij})=0$), the function $f^0(p,t,i,j)$ in the zone of integration $\vec{r}_{ij}$ is nearly constant. Therefore

$$f(p, t)=f^{\circ}(p, t)-v_0\sum_{i<j}w_{pt}(i, j)\,, \tag{12}$$

$$v_0=\int_{-\infty}^{+\infty}\varphi(\vec{r}_{ij})\,\vec{dr}_{ij}=\int_{-\infty}^{+\infty}\left[1-e^{-\frac{u(\vec{r}_{ij})}{RT}}\right]\vec{dr}_{ij}\,, \tag{13}$$

$$w_{pt}(i, j)=\int_{-\infty}^{+\infty}f_0^{\circ}(p, t, i, j)\,\vec{dr}_i, \tag{14}$$

$$f_0^{\circ}(p, t, i, j)=|\,r_{ij}=0 f^{\circ}(p, t, i, j). \tag{15}$$

The constant V_0 which has the dimension of volume may be regarded as the effective excluded volume of a segment. In particular, if the segments are regarded in approximation as solid spheres of diameter d_0, then $V_0=(4\pi/3)d_0^3$.

The magnitudes w_{pt} (i,j) which represent the probabilities of collision of the segments i and j of a Gaussian chain at set locations of the segments p and t, can readily be calculated fromequations (14) and (15). Assigning the location of the origin of the coordinates to segment p for simplicity's sake, we obtain

$$w_{pt}(i, j)=\left(\frac{A}{\pi^3}\right)^{3/2}e^{-\gamma r_{pt}^2}. \tag{16}$$

For six possible sequences of segments i, j, p, t along the chain: 1) $i<j\leqslant p, t$; 2) $p<t\leqslant i<j$; 3) $i\leqslant p<j\leqslant t$; 4) $p<i<t<j$; 5) $i<p<t<j$; 6) $p\leqslant i<j\leqslant t$ we have

$$\gamma_1=\gamma_2=\alpha_{pt}\,;\quad \gamma_3=\frac{(\alpha_{ip}+\alpha_{pj})\alpha_{jt}}{\alpha_{ip}+\alpha_{pj}+\alpha_{jt}}\,;$$
$$\gamma_4=\frac{\alpha_{pi}(\alpha_{it}+\alpha_{tj})}{\alpha_{pi}+\alpha_{it}+\alpha_{tj}}\,;\quad \gamma_5=\alpha_{pt}+\gamma_3\,;\quad \gamma_6=\frac{\alpha_{pi}\,\alpha_{jt}}{\alpha_{pi}+\alpha_{jt}} \tag{17}$$

and

$$A_1=A_2=\alpha_{ij}\alpha_{pt};\quad A_3=\frac{\alpha_{ip}\,\alpha_{pj}\,\alpha_{jt}}{\alpha_{ip}+\alpha_{pj}+\alpha_{jt}}\,;$$
$$A_4=\frac{\alpha_{pi}\,\alpha_{it}\,\alpha_{tj}}{\alpha_{pi}+\alpha_{it}+\alpha_{tj}}\,;\quad A_5=\alpha_{pt}\,\gamma_3\,;\quad A_6=\alpha_{ij}\gamma_6 \tag{18}$$

where

$$\alpha_{nm}=\alpha_{mn}=\frac{3}{2(\bar{r}^2_{nm})_0}=\frac{3}{2\,|m-n|\,a^2}. \tag{19}$$

From equation (12) we find:

$$\bar{r}^2_{pt}=(\bar{r}^2_{pt})_0+\sum_{i<j}\Delta_{ij}(p,t), \tag{20}$$

where

$$\Delta_{ij}(p,t)=v_0\left[(\bar{r}^2_{pt})_0\int_0^\infty w_{pt}(i,j)\vec{dr}_{pt}-\int_0^\infty w_{pt}(i,j)\,r^2_{pt}\,\vec{dr}_{pt}\right] \tag{21}$$

= increase of $\bar{r}^2_{pt}$, conditioned by the interaction of the i^{th} and j^{th} chain segments. By using equations (16)–(19), we find,

$$\Delta_{ij}=\frac{v_0}{a}\left(\frac{3}{2\pi}\right)^{3/2}\frac{\beta_{ij}}{(j-i)^{3/2}}, \tag{22}$$

where for the six sequences given above

$$\beta^{(1)}_{ij}=\beta^{(2)}_{ij}=0;\quad \beta^{(3)}_{ij}=(j-p)^2;\quad \beta^{(4)}_{ij}=(t-i)^2;$$
$$\beta^{(5)}_{ij}=(t-p)^2;\quad \beta^{(6)}_{ij}=(j-i)^2. \tag{23}$$

Substituting equation (22) in equation (23) and summating over i and j, we obtain (disregarding the terms of the order of unity):

$$\bar{r}^2_{pt}=(\bar{r}^2_{pt})_0+\sum_{q=1}^{6}S_q(p,t), \tag{24}$$

where

$$S_1=\sum_{j=1}^{p}\sum_{i=0}^{j-1}\Delta^{(1)}_{ij}=0;\quad S_2=\sum_{j=t+1}^{N}\sum_{i=t}^{j-1}\Delta^{(2)}_{ij}=0;$$

$$S_3=\sum_{i=0}^{p}\sum_{j=p+1}^{t}\Delta^{(3)}_{ij}=\frac{v_0}{a}\left(\frac{3}{2\pi}\right)^{3/2}\left[\frac{4}{9}(t-p)^{9/2}-\frac{4}{9}t^{9/2}-\frac{32}{9}p^{9/2}+\frac{8}{3}pt^{7/2}+\frac{4}{3}\frac{p^2}{t^{1/2}}\right];$$

$$S_4=\sum_{i=p+1}^{t-1}\sum_{j=t+1}^{N}\Delta^{(4)}_{ij}=\frac{v_0}{a}\left(\frac{3}{2\pi}\right)^{3/2}\left[\frac{4}{9}(t-p)^{9/2}-\right.$$
$$\left.-\frac{4}{9}(N-p)^{9/2}-\frac{32}{9}(N-t)^{9/2}+\frac{8}{3}(N-t)(N-p)^{7/2}+\frac{4}{3}\frac{(N-t)^2}{(N-p)^{1/2}}\right];$$

$$S_5=\sum_{i=0}^{p-1}\sum_{j=t+1}^{N}\Delta^{(5)}_{ij}=\frac{v_0}{a}\left(\frac{3}{2\pi}\right)^{3/2}\frac{4}{3}\left[(t-p)^{5/2}-\frac{(t-p)^2}{(N-p)^{1/2}}+\frac{(t-p)^2}{N^{1/2}}-\frac{(t-p)^2}{t^{1/2}}\right]; \tag{25}$$

The sums S_1–S_6 express the contributions of the interactions of the various parts of the chain to the increase in $\bar{r}^2_{pt}$ as a result of the volume effects. It follows from equation (25) that the internal interactions in the chain "tails" (sums S_1 and S_2, corresponding to the cases $i,i<p$ and $i,j>t$) do not affect $\bar{r}^2_{pt}$ as would

have been expected. The sums S_3 and S_4 take into account the interaction of the "centre" of the chain with its "tails", the sum S_5 the interaction of the "tails", and the sum S_6 the internal interactions in the "centre" of the chain.

In the particular case where $p=0$ and $t=N$ equations (24) and (25), making allowance for equation (4), yield the general expression (3) for $\overline{r_{0N}^2}=\overline{h^2}$. From equations (24) and (25) can also be obtained an equation for the mean square radius of the chain inertia:

$$S_6=\sum_{j=p+1}^{t}\sum_{i=p}^{j-1}A_{ij}^{(6)}=\frac{c_0}{a}\left(\frac{3}{2\pi}\right)^{3/2}\frac{4}{3}(t-p)^{9/2}. \qquad \overline{R^2}=\frac{1}{N^2}\sum_{p<t}\overline{r_{pt}^2}=\overline{R_0^2}+\sum_{q=1}^{6}Q_q, \tag{26}$$

where $\overline{R_0^2}=\overline{h_0^2}/6=Na^2/6$, and the sums Q_q are the values of the sums S_q averaged over all p and t values of the sums S_q. We have $Q_q=B_q z\overline{R_0^2}/105$, where $B_1=B_2=0$, $B_3=B_4=16$, $B_5=6$ and $B_6=96$.

From this follows the widely known equation for $\overline{R^2}$ [9], [11]:

$$\overline{R^2}=\overline{R_0^2}\left(1+\frac{134}{105}z\right). \tag{27}$$

The derivation of equation (27) given above makes it possible to determine the influence of the interactions of various parts of the chain on its dimensions. It follows from the values of B_q that the distance between any two pairs of chain segments on average (over all the pairs of segments) will depend chiefly (for 72 per cent) on the internal interactions in the segment linked to this pair of segments. The interaction of this segment with each "tail" of the chain will contribute 12 per cent of the total effect, and the interactions of the "tails", 4 per cent at most.

3. DISTRIBUTION FUNCTION FOR THE END-TO-END DISTANCE

The distribution function for the distance between two arbitrary chain segments $f(\vec{r}_{pt})$ can be derived by substituting equations (16) in equation (12)*; unfortunately summation (or integration) over i and j is impossible to accomplish, generally speaking. However, for the case where $p=0$ and $t=N$, i.e, $r_{pt}=h$, such a summation presents no difficulty. If we substitute equation (16) with A_6 and γ_6 in equation (12), use equation (19), interpolate instead of i a new variant $k=j-i$, change the order of the summation and summate over j, we obtain:

$$f(h)=f_0(h)-\left(\frac{3}{2\pi}\right)^3\frac{v_0}{a^6}\sum_{k=1}^{N}\frac{1}{k^{3/2}(N-k)^{3/2}}\,e^{-\frac{3h^2}{2(N-k)a^2}}. \tag{28}$$

* Because we took point p as the origin of our coordinates, the function $f(p, t)$ reduces to $f(\vec{r}_{pt})$.

Replacing summation by integration and interpolating instead of k a new variant $t=3h^2/2(N-k)a^2-3h^2/Na^2$, we obtain (neglecting terms of the order $z/\sqrt{N}$):

$$f(h)=f_0(h)\left[1-2\sqrt{N}\,z+\sqrt{6\pi}\,z\frac{h}{(\bar{h}_0^2)^{1/2}}\right]=f_0(h)\cdot F(h), \tag{29}$$

where $f_0(h)=(3/2\pi\bar{h}_0^2)^{3/2}\exp\left[-3h^2/2\bar{h}_0^2\right]F(h)$, denotes the relative number of configurations destroyed by the volume effects. Comparison of the mean value of this magnitude $F_N=1-2\sqrt{N}\,z+4z$ with the result which follows at low values of z from Flory's theory [2] ($F_N=1-3\sqrt{3}z/2$), reveals that the actual number of destroyed chain configurations is substantially less than the number based on Flory's theory owing to the presence of a term proportional to $\sqrt{N}z$. However, the difference is not apparent at intermediate chain dimensions because the corresponding term is independent of h. Observe too that the precise equation for F_N (unlike Flory's equation) is in keeping with the obvious inequality $F_{2N}<F_N^2$.

After normalization equation (29) can be written:

$$W(h)=W_0(h)\left[1+\sqrt{6\pi}\,z\frac{h}{(\bar{h}_0^2)^{1/2}}-4z\right], \tag{30}$$

where $W_0(h)=f_0(h)$. An analogous equation was derived (by a non-strict method by Peterlin [23] who represented F(h) as a power series in h and assumed that the coefficient h^m must be proportional to z^m. Consequently for $W(h)$ Peterlin's assumption is justified (as will be seen later this is not so for the general case $W(\vec{r}_{pl})$). Equation (30) also follows from the equation for $W(h)$ derived by James [8] which is not restricted to low values of z. This shows that James' method is strict at low z values although at high z values it yields false results (in particular the coefficient at z^2 in the series expansion over z of James' equation for h^2 is wrong both in magnitude and in sign [11]).

Observe that the distribution function (30) differs markedly from the effective Gaussian distribution function corresponding to the same value of $\bar{h}^2$ (the real distribution function decreases more quickly at higher values of h and increases more slowly at low values of h).

The decrease in the distribution function has one effect in particular, viz. it reduces the difference between the extremely probable value (h_m) and the mean quadratic value h in comparison with the Gaussian function. From equation (30) it follows that

$$h_m^2=\frac{2}{3}\bar{h}_0^2(1+\sqrt{\pi}z)=\frac{2}{3}\bar{h}^2(1+0{\cdot}44z) \tag{31}$$

(for the Gaussian function $h_m^2=(2/3\bar{h}^2)$. As an illustration of the difference between the distribution function (30) and the effective Gaussian function, note that $(\overline{1/h})=(\overline{1/h})_0(1-0.86z)$, *but* $(\overline{1/h})_{gauss}=(\overline{1/h})_0(1-0.67z)$.

4. DISTRIBUTION FUNCTION FOR THE DISTANCE BETWEEN AN ARBITRARY PAIR OF CHAIN SEGMENTS

On analogy with equation (29) we shall look for an approximate expression for $\vec{f(r_{pt})}$ in the form of a product of a Gaussian function in a series over $r_{pt}/(\overline{r_{pt}^2})_0^{1/2}$, where the coefficient for the m^{th} term of the series (in terms of p and t) is proportional to z^m. As we saw earlier the function $W(h)$ can be represented strictly in this way. The contribution of an arbitrary pair of segments p and t is thus strictly represented as a function of the interactions of the segments in the "centre" of the chain which has a determinative influence. The contributions of the remaining interactions are described only approximately by such an equation: nevertheless, as we shall see later, this apropximation is adequate for all practical purposes.

Confining ourselves to a term, linear with respect to z and normalizing, we find

$$W(r_{pt}) = W_0(r_{pt}) \left[1 + z\varphi(p, t) \frac{r_{pt} - (\overline{r_{pt}})_0}{(\overline{r_{pt}^2})_0^{1/2}} \right], \tag{32}$$

where the zero indices at r_{pt} denote averaging with the function $W_0(r_{pt})$. To calculate the coefficient $\varphi(p, t)$ we calculate by means of the function $W(r_{pt})$ the magnitude $\overline{r_{pt}^2}$:

$$\overline{r_{pt}^2} = (\overline{r_{pt}^2})_0 \left[1 + \left(\frac{2}{3\pi} \right)^{1/2} \pi z \varphi(p, t) \right]. \tag{33}$$

The coefficient $\varphi(p,t)$ can be calculated from a comparison of the magnitude $\overline{r_{pt}^2}$ calculated by means of the function $W(r_{pt})$ with the result of the direct calculation of $\overline{r_{pt}^2}$ from equations (24) and (25). Finally, we obtain

$$W(r_{pt}) = W_0(r_{pt}) \left[1 - 3\psi(p, t) + \frac{1}{\pi} \left(\frac{3\pi}{2} \right)^{1/2} \psi(p, t) \frac{r_{pt}}{(\overline{r_{pt}^2})_0^{1/2}} \right], \tag{34}$$

where

$$\psi(p, t) = \frac{1}{\sqrt{N}\sqrt{t-p}} \sum_{q=1}^{6} S_q.$$

The approximate equation (34) is a comparatively ready means of calculating the mean values of the various functions in terms of r_{pt} which cannot always be determined by the precise method described above. In particular, from equation (34), we obtain

$$\frac{1}{N^2} \sum_{p<t} \overline{r_{pt}^4} = 5 (\overline{R_0^2})^2 (1 + 2{\cdot}42z) \tag{35}$$

and

$$\frac{1}{N^2} \sum_{p<t} \left(\overline{\frac{1}{r_{pt}}} \right) = \frac{4}{3\sqrt{\pi}} \frac{1}{(R_0^2)^{1/2}} (1 - 0{\cdot}54z). \tag{36}$$

The first magnitude determines the initial curvature of the plot pertaining to the angular intensity distribution of scattered light, and the second is the fric-

tion constant of the macromolecule. From the strict theory explaining these phenomena and developed respectively in papers [21, 22] and [24], follow the coefficients at z in equations (35) and (36) viz. 2·33 and 0·61 respectively. It will be apparent that the proposed approximate method in these cases gives a satisfactory approximation (the discrepancy with respect to the accurate value is 3·5 and 12 per cent respectively). However, other approximate methods based on the use of the effective Gaussian distribution function for r_{pt} [17], [19], [25] and [26] or on deriving $z \times \varphi(p,t)$ from $z \times \varphi(O,N)$ by the substitution of $(t-p)$ for the latter N [27], [28], yield greatly inferior results (coefficients for z in equation (36) are respectively 0·42 and 0·33 which makes an error of 31 and 46 per cent).

5. THE INFLUENCE OF VOLUME EFFECTS ON CHAIN STRETCHING

As has been demonstrated by Vol'kenshtein and the author [29] the statistical sum of a chain in the field of an external potential force may be written:

$$Z = Z_0 \overline{\left(\frac{\mathrm{sh}\,(\varkappa h)}{\varkappa h}\right)}, \tag{37}$$

where $\varkappa = f/kT$, Z_0 = the value of Z at $f \to 0$ and averaging on the right in equation (37) is carried out in the absence of an external force. Using equation (30), we obtain as a result of elementary integration and simple transformations:

$$\frac{Z}{Z_0} = e^{\xi^2}\left\{1 - 4z + 2ze^{-\xi^2} + \sqrt{\pi}\, z\left(\frac{1}{\xi} + 2\xi\right)\Phi(\xi)\right\}, \tag{38}$$

where

$$\xi = \varkappa(\overline{R_0^2})^{1/2} = \frac{\sqrt{N}}{6}\,\frac{fa}{kT}, \tag{39}$$

and

$$\Phi(\xi) = \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-t^2}\, dt$$

which is an integral of probability.

By means of equation (38) it is possible to compute the mean value for the projection of the chain length vector in the direction of the external potential force:

$$\bar{x} = \frac{\partial \ln (Z/Z_0)}{\partial \varkappa} = 2(\overline{R_0^2})^{1/2}\left\{\xi + \frac{z}{\xi}\, e^{-\xi^2} + \sqrt{\pi}\, z\left(1 - \frac{1}{2\xi^2}\right)\Phi(\xi)\right\}. \tag{40}$$

At $\xi \ll 1$ we obtain from equation (40), using equation (39):

$$\bar{x} = 2(\overline{R_0^2})^{1/2}\,\xi\left(1 + \frac{4z}{3}\right) = \frac{\overline{h^2}}{3kT} f. \tag{41}$$

Equation (41) concurs with the general expression derived by Guth and Mark [30] for freely bonded chains and by Vol'kenshtein and the author [29]

for arbitrary chains. However, whereas for chains in the absence of volume effects the extent to which equation (41) is applicable depends upon the condition $fa/kT \ll 1$, for chains with volume effects the equation is operative only provided $f(\overline{R_0^2})^{1/2}/kT \ll 1$. If compliance with the first condition ceases only at very high forces which extend the chain to dimensions comparable with its maximum length, then the second condition is invalid for forces lower by a factor $N^{-1/2}$ at which orientation sets in the external force field of the chain as a whole.

At $\xi \gg 1$ equation (40) will give

$$\bar{x} = 2(\overline{R_0^2})^{1/2}(\xi + \sqrt{\pi} \cdot z) \tag{42}$$

or, discarding other than ξ order terms (since $\xi \gg 1$):

$$\bar{x} = 2(\overline{R_0^2})^{1/2}\xi = \frac{\overline{h_0^2}}{3kT} f. \tag{43}$$

Comparison of equations (41) and (43) reveals that if, at very slight external forces, the gradient of the plot of $\bar{x}$ against f is determined by the true mean quadratic dimensions of the chain, then for a very small increase in the force (sufficient to orient the chain) further stretching is governed by the mean quadratic dimensions of the chain in an ideal solvent. Observe that at large values of N the condition $\xi \gg 1$ is, of course, entirely in agreement with $fa/kT \ll 1$, a condition which implies the possibility of discarding the corrections associated with greater stretching of the chain. From equation (40) and its limiting cases, viz. equations (41) and (43), it follows that the volume effects lead to a non-linear plot for the projection of the chain length in the direction of the external force against the value of the applied force in the small extension range. Bear in mind that this conclusion is of direct relevance to the potential forces only.

6. APPROXIMATE STATISTICAL THEORY OF VOLUME EFFECTS

The strict theory pertaining to the influence of the volume effects on the dimensions of polymer chains is only operative close to the θ-point. Good solvents necessitate the approximate theory formulated by Flory and co-workers [2–5] and refined by Vol'kenshtein and the author [15, 16] who studied the non-Gaussian nature of the distribution function and found:

$$W(h) = C \cdot W_0(h) \cdot \exp\left[-3\sqrt{6}\,\frac{z}{\pi^2}\,\frac{1}{(1+h^2/h_0^2)^{1/2}}\right] \tag{44}$$

(C = normalizer constant). Equation (44) accounts for the sharpening of the distribution function maximum (in comparison with the effective Gaussian function) mentioned above. At low h values the equation somewhat understates this effect (in comparison with the accurate distribution function) and at high values of h it slightly overstates the effect.

Interpolating the new variable $t=\overline{h}/(\overline{h_0^2})^{1/2}$ and using the general expression for $h^2=\alpha^2\overline{h_0^2}$ over $W(h)$, we obtain from equation (44) the following integral equation for α:

$$\alpha^2=\frac{\int_0^\infty \exp\left[-\frac{3}{2}t^2-\frac{3\sqrt{6}\,z}{\alpha^3}\cdot\frac{1}{(1+t^2/\alpha^2)^{3/2}}\right]t^4dt}{\int_0^\infty \exp\left[-\frac{3}{2}t^2-\frac{3\sqrt{6}\,z}{\alpha^3}\cdot\frac{1}{(1+t^2/\alpha^2)^{3/2}}\right]t^2dt}. \tag{45}$$

Equation (45) fixes α as a function of z, replacing Flory's equation (7); however, integration on the right of equation (45) by analogous means is impossible. Papers [15, 16] cited various approximate expressions as replacements for equation (45). Below we shall examine this equation in detail.

At $z\ll 1$ we derive from equation (45):

$$\alpha^2=1+\frac{54z}{\sqrt{\pi}}\left\{\int_0^\infty e^{-\frac{3}{2}t^2}\frac{t^2dt}{(1+t^2)^{3/2}}-\int_0^\infty e^{-\frac{3}{2}t^2}\frac{t^4dt}{(1+t^2)^{5/2}}\right\}. \tag{46}$$

Numerical integration will give

$$\alpha^2=1+1{\cdot}15z\,. \tag{47}$$

Consequently the coefficient with a linear term in the series expansion of α^2 over z developed in [15, 16] differs by only 13 per cent from its accurate value ($4/3=1{\cdot}33$) whilst Flory's theory will give a value for the coefficient ($3\sqrt{2/2}=2{\cdot}60$) differing from the accurate value by nearly a factor of 2.

In order to study α as a function of z we find from equation (44) an extremely likely value of h. We have:

$$\alpha^5-\frac{2}{3}\frac{\alpha^3}{\kappa^2}=\frac{3\sqrt{6}\,z}{(1+\kappa^2)^{3/2}}\,, \tag{48}$$

where $\kappa^2=h^2m/\overline{h^2}$. Were the function $W(h)$ Gaussian we should have $\kappa^2=2/3$ and equation (48) would give

$$\alpha^5-\alpha^3=81/25\sqrt{2/5}\,z=2{\cdot}06z\,. \tag{49}$$

In actual fact, however, the volume effects accentuate the distribution function and therefore $\kappa^2>2/3$ (cf. equation (31)). It can readily be demonstrated that in the limiting case of very strong volume effects ($z\to\infty$), $\kappa\to 1$, which will give:

$$\alpha^5=\frac{3\sqrt{3}}{4}\,z, \tag{50}$$

i.e. the coefficient at z is exactly twice as small as in Flory's equation (7).

At intermediate z values κ^2 can be written in the form $\kappa^2=(2/3)\,[1+\delta(z)]$, where, as z increases from zero to infinity, $\delta(z)$ increases monotonously from

zero to $\frac{1}{2}$. Substituting this expression in equation (48) and making use of the fact that $\delta(z) \leqq {}^1/_2[1+\frac{2}{3}\delta(z)]^{3/2} \cong 1+\delta(z)$, we obtain

$$\alpha^3 - \alpha^2 = \varphi(z)z, \tag{51}$$

where

$$\varphi(z) \cong 2{\cdot}06 - \frac{\alpha^3\delta(z)}{z} \tag{52}$$

Comparison of equation (51) with equations (47) and (50) reveals that at $z \to 0$ $\varphi(z) \to 1{\cdot}15$, and at $z \to \infty$ $\varphi(z) \to 3\sqrt{3}/4 = 1{\cdot}30$. The numerical derivation of the integral equation (45) at $z=2$ gave $\alpha = 2{\cdot}377$, to which corresponds $\varphi(z) = 1{\cdot}17$. Hence, as it rises from zero to inffnity, $\varphi(z)$ increases very slightly from 1·15 to 1·30. In the range $\alpha = 1{\cdot}0$–$1{\cdot}5$ with which we are generally concerned in practice it can be assumed with sufficient accuracy that $\varphi(z) = 1{\cdot}15$.

We shall see that the approximate statistical theory pertaining to the volume effects which is formulated in [15] and [16] results in an equation of the same type as Flory's (7) although with the value of the constant on the right nearly twice as small. As previously stated the series expansion of equation (51) over z leads to an equation almost coincident with the accurate equation (3).

It must be noted that the quantitative experimental verification of equations (3) or (8) relating α through z to the thermodynamic parameters of the system (cf. equation (6)), still remains largely unsolved. Stockmayer's derivation [14] based on the experiments of Flory and co-workers [31], [32] concerning the validity of equation (3), and not of (8), is based on the assumption of proportionality between the intrinsic viscosity and the volume of the macromolecule. Nonetheless, as shown by theory [19, 20] and experiment [33] this derivation is false because Flory's constant depends on α, and this relationship is particularly clearly expressed close to the θ-point, viz. precisely in the range in which the experimental findings of [31] and [32] used by Stockmayer are obtained. Analogous critical considerations also apply to the comparison in papers [4] and [34] of equations (7) or (53) with experimental findings in the domain of good solvents. We are aware of only one attempt at a quantitative comparison of equation (3) with experiment to which these limitations do not apply, i.e. the paper by Kurata and Yamakawa [26] in which are used values of α derived from experiments based on Zimm's light scattering method. This attempt gave excellent results but it needs to be borne in mind that any comparison of the theory of volume effects with experiment necessitates determination of the thermodynamic parameter ψ_1 from experiments on the temperature dependence of the second virial coefficient A_2. This determination can be carried out independently of the model theories of A_2 only in the immediate neighbourhood of the θ-point where the temperature dependence of A_2 is difficult to determine owing to the scattering of the experimental findings. In particular it can readily be seen that in every case for one of the two systems discussed in paper [27] equation (8) would not give worse agreement with ex-

periment than equation (3). We therefore assume that for a definitive quantitative verification of equation (3) further detailed measurements of the temperature dependences of $\overline{R^2}$ and A_2 close to the θ-point are required.

A further variant of the approximate statistical theory of the volume effects was recently put forward by Krigbaum [35]. In deriving his equation for $W(h)$ this author, in common with the authors of the foregoing theory, took as his starting point the equation for the mean square radius of the inertia of a Gaussian chain with an end-to-end distance h : $R_h^2=\overline{h_0^2}/12+h^2/12$. However, Krigbaum erroneously assumed this equation also to be valid taking into account the volume effects whereas here it needs to be replaced by the expression $\overline{R_h^2}=\overline{h^2}/12+h^2/12$ [15, 16]. Hence in Krigbaum's distribution function stands $(1+h^2/h_0^2)^{3/2}$. instead of $\alpha^3(1+h^2/h^2)^{3/2}$ (cf. equation (44)). Moreover in his theory the chain is assumed to be broken down into sub-chains so that instead of the factor z contained in equation (44) Krigbaum's distribution function contains a factor dependent on the number of sub-chains in the macromolecule, i.e. a value whose physical significance, as pointed out by the author himself, remains obscure and which cannot be determined by an independent method.

7. INFLUENCE OF HETEROGENEOUS SWELLING OF THE SPHERE

As pointed out by Zimm, Stockmayer and Fixman [9] an approximate equation for α of Flory's type (7) may be derived from the precise equation (3) on the assumption that the volume effects produce a α-fold increase in the length of the chain segment. Actually, replacing in equation (3) the parameter z (proportional to a^{-3}) by z/α^3, we obtain the equation

$$\alpha^5-\alpha^3=4z/3, \tag{53}$$

which differs from Flory's equation (7) only by a numerical factor and is practically identical with our equation (51).

In fact, however, the volume effects lead to non-Gaussian distribution functions for $r_{\mu\iota}$ so that their influence on the dimensions of the macromolecule cannot be described by an increase in the effective length of a segment (the influence of the volume effects on the various parameters of the macromolecule with the dimension of length differs).

Consequently the parameter z in equation (3) must be replaced not by z/α^3 but by z/α_{eff}^3 where α_{eff} is not, in general, equal to α. At low z values $\alpha_{eff}^2=1+\beta z$, where $\beta\neq 4/3$. To determine β we use Fixman's equation [11];

$$\alpha^2=1+\frac{4z}{3}-2{\cdot}08\,z^2. \tag{54}$$

Furthermore from equation (3) we obtain (accurate to z^2 order terms):

$$\alpha^2=1+\frac{4z}{3\alpha_{eff}^3}=1+\frac{4z}{3}-2\beta z^2, \tag{55}$$

hence $\beta = 1{\cdot}04$, i.e.

$$\alpha_{eff}^2 = 1 + 1{\cdot}04\, z, \tag{56}$$

so that $\alpha_{eff} < \alpha$. At higher z values the equation

$$\alpha_{eff}^5 - \alpha_{eff}^3 = 1{\cdot}04\, z, \tag{57}$$

which has been derived from equation (56) by substituting z/α_{eff}^3 for z, is valid for α_{eff}.

Thus, taking into account the heterogeneous swelling of the sphere, we obtain for $\alpha^2 = \overline{h^2}/\overline{h_0^2}$ the equation

$$\alpha^3 - 1 = 1{\cdot}28\,(\alpha_{eff}^2 - 1), \tag{58}$$

where α_{eff} is expressed by equation (57). Unlike equation (53), equation (58) will correctly give not one, but two coefficients in the series expansion of α^2 over z and should also give a better approximation at high z values since it makes allowance for the heterogeneity of the swelling of the sphere. Equation (58) can be written in the form

$$\alpha^5 - \alpha^3 = \frac{4z}{3} \cdot \frac{\alpha^3}{\alpha_{eff}^3}. \tag{59}$$

At low z values $\alpha^3/\alpha_{eff}^3 = 1 + 0{\cdot}44\, z$ at $z \to \infty$ $\alpha^3/\alpha_{eff}^3 \to (4/3 - 1{\cdot}04)^{-1} = 1{\cdot}45$

Thus, as z increases from zero to infinity α^3/α_{eff}^3 increases by almost a factor of $1\frac{1}{2}$. Consequently, unlike Flory's theory, equation (59) gives the increase of $(\alpha^5 - \alpha^3)/z$ associated with that of z. In particular $(\alpha^5 - \alpha^3)/\sqrt{M}$ must increase for higher molecular weight of the polymer whereas according to Flory's theory it must remain constant.

α is plotted as a function of z in accordance with equation (59) (taking equation (57) into account) in Fig. 1 (continuous curve). For comparison the broken

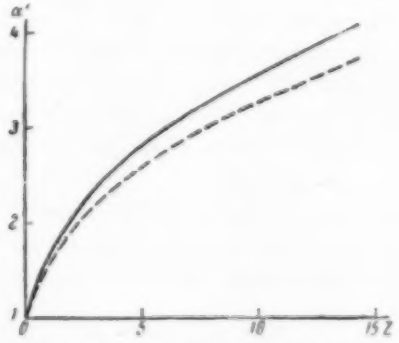

FIG. 1. α plotted against z for equations (57) and (59) of the present paper (full line plot) and for the amended Flory equation (53) (broken line plot).

line curve expresses α as a function of z in accordance with Flory's equation corrected to accord with the results of the strict statistical theory (i.e. by means

of equation (53)). We shall see that correction for the heterogeneity of the swelling of the sphere leads to an increase in the values of α given by the theory (for a given value of z).

From equation (57) and (59) is derived the following equation for the power exponent ε as a function of $\alpha^2 \sim M^\varepsilon$;

$$\varepsilon = \frac{1}{5} \cdot \frac{1-1/\alpha^3}{1-3/5\alpha_{eff}^2}. \tag{60}$$

From Flory's equation $\alpha^5 - \alpha^3 = \text{const.} \times z$ we have 19

$$\varepsilon_\varphi = \frac{1}{5} \cdot \frac{1-1/\alpha^3}{1-3/5\,\alpha^3} \tag{61}$$

Since $\alpha_{eff} < \alpha$, $\varepsilon > \varepsilon_\varphi$ at any finite value of α but the difference between them is slight.

The merits of the modified Flory equation (53) and the equation proposed on the present paper (59) can be assessed experimentally by accurate measurement of the relationship between α and M. In the work carried out by Flory *et al.* over a wide range of M values (from 10^4 to 10^6) it was found that for poly-*iso*butylene in cyclohexane and di*iso*butylene [5], [31], [36] the magnitude $(\alpha^5 - \alpha^3)/\sqrt{M}$ as a function of M has a slight maximum, and for polystyrene in benzene [5], [38] it increases directly with M. The calculations of $(\alpha^5 - \alpha^3)/\sqrt{M}$ performed by us on the basis of experimental results derived from light scattering (by Zimm's method) for polystyrene in toluene [38] and polyvinyl acetate in methyl ethyl ketone [39] seem to indicate that $(\alpha^5 - \alpha^3)/\sqrt{M}$ increases directly with M (Fig. 2) although definitive conclusions cannot yet be inferred from the limited experimental information. (Findings of a more indirect nature

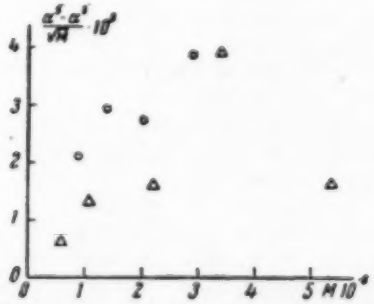

FIG. 2. $(\alpha^5 - \alpha^3)/\sqrt{M}$ plotted against M for polystyrene in toluene [40] (triangles) and for polyvinyl acetate in methyl ethyl ketone [4] (circles).

derived from the intrinsic viscosity and from light scattering by Debye's method are, in our view, unsuitable for a precise check on the theory).

The author thanks Iu. E. Eizner, A. Ezrielev and F. Dobrovol'skii for their assistance.

CONCLUSIONS

(1) The distribution functions for the distances between different pairs of segments in polymer chains (for the end-to-end distance in particular) accounting for the volume effects are essentially non-Gaussian.

(2) The volume effects lead to a non-linear relationship between the chain length projection in the direction of the applied external potential force and the magnitude of that force.

(3) The volume effect theory previously developed by Vo'lkenshtein and the author which accounts for the non-Gaussian nature of the distribution function for the end-to-end distance is in far better agreement with the strict theory than Flory's.

(4) When allowance is made for the swelling of the sphere under the influence of the volume effects it leads to a radical alteration in Flory's theory, in particular to the magnitude of $(\alpha^5-\alpha^3)/\sqrt{M}$ increasing directly with M and this accords with experiment.

Translated by G. CAMERON

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VOL.
1
1960

INTERNAL ROTATION AND PHYSICAL PROPERTIES OF POLYMER CHAINS—XVI. THE MEAN OPTICAL ANISOTROPY OF ISOTACTIC VINYL POLYMER MOLECULES*

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(*Received* 19 *March* 1959)

INTRODUCTION

THE theory of the mean optical anisotropy of polymer chains, formulated for the case of freely linked chains [1], has been extended to chains with hindered rotation in an approximation where the rotations of adjacent segments [2–5] or the rotations of segments of adjacent monomer units [6] were assumed independent. In real chains of linear polymers of the type $(-CH_2-CR'R''-)_n$ (R′ and/or R″ are compact side-chains) the rotations in the adjacent monomer units (configuration of monomer units) are not independent owing to the interactions between the adjacent methylene groups as well as the interactions between the nearest, non-adjacent R-groups.

In the present paper a method of calculating the optical anisotropy of such polymers is described. It combines the method developed by Gotlib [2, 4] of averaging the tensor characteristics of chains with independent rotation about the individual bonds and Izing's version of the matrix method employed in the theory of ferromagnetism (cf. e.g. [7]) which enables the correlation between the rotations to be taken into account [8, 9]. The method is based on the rotation-isomeric polymer chain model constructed by Vol'kenshtein [10] and on the procedure proposed by Ptitsyn and Sharonov [11] to ascertain the possible configuration of monomer units from the configuration of the polymer chains in the crystal. A valence-optical scheme (cf. e.g. [12]) which assumes additivity of the bond polarizability tensors is used in the calculation. It is further assumed that the optical anisotropy of the monomer units is independent of their configuration; this corresponds to the case where the side-chains R are axially symmetrical or where the rotation in the side-chains is independent of the rotation in the principal chain. The numerical values of isotactic polymers crystallizing in the form of 3_1 spirals are calculated.

* Vysokomol. soedin. **1**: No. 5, 748–757, 1959.

METHOD OF CALCULATION

As pointed out elsewhere [4, 6] the mean optical anisotropy of the chain of a $(-CH_2-CR'R''-)_n$ type homopolymer may be written in the form

$$\Delta A = \sum_{r=1}^{3}\sum_{s=1}^{3} \alpha_{rs} S_{rs}. \tag{1}$$

where

$$S_{rs} = S_{sr} = \frac{9}{10}\,\frac{1}{h^2}\left\{ l'^2 \sum_{k=1}^{n}\sum_{l=1}^{n} \overrightarrow{(e_z^{(l)}} \overrightarrow{e_r^{(k)}})\,\overrightarrow{(e_s^{(k)}} \overrightarrow{e_z^{(m)}}) - \frac{1}{3}\, n h^2 \delta_{rs} \right\}. \tag{2}$$

$$S\text{pur} = S = 0. \tag{3}$$

Here α_{rs} $(r, s = X, Y, Z)$ are tensor components of the polarizability of the monomer unit in a local system of coordinates associated with it (i.e. with the two members $CH_2-CR'R''$ and $CR'R''-CH_2$); the tensor is averaged over the rotation in the side-chain which is independent of the rotation in the principal chain. δ_{rs} is Kroneker's notation, $\vec{e}_r^{(k)}$, $\vec{e}_z^{(l)}$ are unit loci respectively of the k and l local systems of coordinates that are constructed in conformity with the stereoisomerism of the monomer units and the directions of the Z_k axes are chosen such that

$$l' \sum_{k=1}^{n} \vec{e}_z^{(k)} = \vec{h}. \tag{4}$$

where l' = length of monomer units, $\vec{h}$ = vector of length of macromolecule, n = degree of polymerization.

It can readily be shown that

$$\alpha_{xz} = \alpha_{yz} = 0. \tag{5}$$

Hence, by altering the direction of all the Z axes we shall pass from a d-isomer in the right-hand coordinate system to an l-isomer in the left-hand coordinate system with α_{xz} and α_{yz} changing sign and since the polarizability tensors of the d and l-isomers in the relevant coordinate system must be identical, $\alpha_{xz} = \alpha_{yz} = 0$.

The internal energy of a polymer chain in which the configurations of the adjacent monomer units are correlated can be written in the form (neglecting chain-end influence):

$$U(\varphi_1, \varphi_2, \ldots, \varphi_N) = U(\Omega_1, \Omega_2, \ldots, \Omega_n) = \sum_{i=1}^{n} U(\Omega_{i-1}, \Omega_i). \tag{6}$$

where φ_i = angle of internal rotation of ith bond about $(i-1)$th, Ω_i = aggregate of internal rotation angles (configuration) of the bonds of the ith monomer unit, $N = 2n$ = number of segments in chain.

If we denote the three loci $\vec{e}_r^{(i)}$ $(r=X, Y, Z)$ in the ith system of coordinates by a column, we shall have for the elements of the sum participating in equation (2) when $l \leqslant k$,

$$\overline{(\vec{e}_z^{(l)}\vec{e}_r^{(k)})\,(\vec{e}_s^{(k)}\vec{e}_z^{(l)})} = \frac{\sum_{\Omega_1}\sum_{\Omega_2}\cdots\sum_{\Omega_n}\prod_{i=1}^{n} g(\Omega_{i-1}, \Omega_i)\,\tilde{\vec{e}}_z \prod_{i=l+1}^{k} S(\Omega_i)\,\vec{e}_r\tilde{\vec{e}}_s \prod_{i=k}^{l+1}\tilde{S}(\Omega_i)\vec{e}_z}{\sum_{\Omega_1}\sum_{\Omega_2}\cdots\sum_{\Omega_n}\prod_{i=1}^{n} g(\Omega_{i-1}, \Omega_i)}. \quad (7)$$

where $S(\Omega_i)$=cosine matrix of angles between the axes of the $(i-1)$th and ith coordinate systems with elements $s_{rs}(\Omega_i)=(\vec{e}_r^{\,i-1}\vec{e}_s^{(i)})$, $\tilde{S}(\Omega_i)$=transposed matrix, $\tilde{\vec{e}}_r$=transposed vector of $\vec{e}_r$ and

$$g(\Omega_{i-1}, \Omega_i)=e^{-\frac{U(\Omega_{i-1}, \Omega_i)}{RT}}. \quad (8)$$

Addition is carried out in (7) for all rotation isomers of monomer units whilst in the case of homopolymers the pattern of rotation isomers is the same for all monomer units.

The magnitudes $g(\Omega_{i-1}, \Omega_i)$ which are transient values independent of i, may be regarded as elements of the matrix G, the order of which is equal to the possible number of configurations f of each of the monomer units. Taking this into account, writing $\Omega_0=\Omega_n$ and assuming that relative to the cyclic transposition of the matrices the trace of their product is invariant, we have

$$\overline{(\vec{e}_z^{(l)}\vec{e}_r^{(k)})\,(\vec{e}_s^{(k)}\vec{e}_z^{(l)})} = \tilde{\vec{e}}_z \frac{S\,\mathrm{pur}\,(G^{n-(k-l)}N^{(k-l)}(r, s))}{S\,\mathrm{pur}\,G^n}\vec{e}_z, \quad (9)$$

where $N^{(k-l)}(r, s)$=hypermatrix of order f, the elements of which, denoted by the numbers of the rotation isomers, are matrices of the third order

$$\{N^{(k-l)}(r, s)\}_{\alpha\beta} = \left[\sum_{\Omega_{l+1}}\sum_{\Omega_{l+2}}\cdots\sum_{\Omega_{k-1}}\prod_{i=l+1}^{k} g(\Omega_{i-1}, \Omega_i)\,S(\Omega_i)\,I_{rs}\prod_{i=k}^{l+1}\tilde{S}(\Omega_i)\right]_{\substack{\Omega_l=\Omega^{(\alpha)}\\ \Omega_k=\Omega^{(\beta)}}}. \quad (10)$$

Here $I_{rs}=(\vec{e}_r\tilde{\vec{e}}_s+\vec{e}_s\tilde{\vec{e}}_r)/2$. It will be apparent that the elements of the hypermatrix $N^{(k-l)}(r, s)$ will depend upon k and l only by their difference.

Reducing matrix G to its diagonal form

$$G=UAU^{-1}, \quad (11)$$

we finally obtain

$$\overline{(\vec{e}_z^{(l)}\vec{e}_r^{(k)})\,(\vec{e}_s^{(k)}\vec{e}_z^{(l)})} \simeq \{N^{(k-l)}(r, s)\}_{11}. \quad (12)$$

where

$$N^{(k-l)}(r, s)=U^{-1}\frac{N^{(k-l)}(r, s)}{\lambda_1^{k-l}}U \quad (13)$$

= a hypermatrix of f order, the elements of which are matrices of the third order, and λ_1 = maximum numerical characteristic of matrix G.

Analogously converting all the elements of the sum of equation (2) and taking into account that [9]

$$\overline{h^2} = l^2 \left[n + 2\vec{e}_z \sum_{k=2}^{n} \sum_{m=1}^{k-1} (W^{k-m})_{11} \vec{e}_z \right], \tag{14}$$

where W = a hypermatrix of f order with elements

$$W_{\alpha\beta} = \frac{\lambda_\alpha}{\lambda_1} \sum_{\Omega_i} \{U^{-1}\}_{\alpha\Omega_i} U_{\Omega_i\beta} S(\Omega_1), \tag{15}$$

we have,

$$S_{rs} = \frac{9}{10} \frac{l^2}{\overline{h^2}} \vec{e}_z \left\{ \sum_{k=1}^{n} \sum_{l=1}^{k} N^{(k-l)}(r, s) + \sum_{l=2}^{n} \sum_{k=1}^{l-1} M^{(l-k)}(r, s) + \right.$$

$$+ 2 \sum_{k=2}^{n} \sum_{l=2}^{k} \sum_{m=1}^{l-1} W^{l-m} N^{(k-l)}(r, s) + 2 \sum_{m=2}^{n} \sum_{l=1}^{m-1} \sum_{k=1}^{l} M^{(l-k)}(r, s) W^{m-l} + \tag{16}$$

$$\left. + 2 \sum_{l=3}^{n} \sum_{k=2}^{l-1} \sum_{m=1}^{k-1} W^{k-m} I_{rs} W^{l-k} - \frac{n}{3} \delta_{rs} \left[n + 2 \sum_{k=2}^{n} \sum_{m=1}^{k-1} W^{k-m} \right] \right\}_{11} \vec{e}_z,$$

where $M^{(l-k)}(r, s)$ = a hypermatrix of f order, the elements of which are third order matrices

$$\{M^{(l-k)}(r, s)\}_{\alpha\beta} = \sum_{\Omega_l} \sum_{\Omega_{l+1}} \cdots \sum_{\Omega_k} \{U^{-1}\}_{\alpha\Omega_l} \prod_{i=l}^{k+1} \widetilde{S}(\Omega_i) I_{rs} \times$$

$$\times \prod_{i=k+1}^{l} g(\Omega_{i-1}, \Omega_i) S(\Omega_i) U_{\Omega_l\beta}. \tag{17}$$

Summing in (16) we shall put the elements of the hypermatrices $N^{(m)}$ and $M^{(m)}$ in the form of a combination of elements of a given matrix raised to the power m. The problem is then reduced to the summation of dual and triple geometrical progressions proceeding from the matrices. Generalizing the method of recurrent relationships proposed by Gotlib [2, 4] we have

$$\{N^{(m)}(r, s)\}_{\alpha\beta} = \frac{\lambda_\alpha}{\lambda_1} \sum_{\Omega_1} \sum_{\Omega_2} \{U^{-1}\}_{\alpha\Omega_1} U_{\Omega_1\Omega_2} S(\Omega_1) \{N^{(m-1)}(r, s)\}_{\Omega_2\beta} \widetilde{S}(\Omega_1). \tag{18}$$

Equation (18) associates the elements of the β column of the hypermatrix $N^{(m)}(r, s)$ with the elements in the same column of the hypermatrix $N^{(m-1)}(r, s)$. We are interested only in the elements of the first column participating in (16). The third order matrix elements that are elements of the hypermatrix $N^{(m)}(r, s)$ are interrelated by the following conditions

$$\sum_{l} \vec{e}_l \{N^{(m)}(r, s)\}_{\alpha\beta} \vec{e}_l = \delta_{rs} \delta_{\alpha\beta} \left(\frac{\lambda_\alpha}{\lambda_1} \right)^m \tag{19}$$

and

$$\vec{e}_l \{N^{(m)}(r, s)\}_{\alpha\beta} \vec{e}_{l'} = \vec{e}_{l'} \{N^{(m)}(r, s)\}_{\alpha\beta} \vec{e}_l. \tag{20}$$

Equation (19) is associated with the orthogonal character of the $S(\Omega)$ matrices. Thus each third order matrix will contain 5 independent elements and the homogeneous system $9f$ of equation (18) on which are superimposed the relations (19) and (20) is convertible into a heterogeneous system $5f$ of independent equations.

We shall write the independent elements of the third order matrices as components of five-dimensional vectors and the combination of all independent elements of the first column of the hypermatrix $N^{(m)}(r, s)$ as an f-dimensional hypervector $\vec{N}^{(m)}(r, s)$, the components of which are fifth order vectors. The recurrent equations (18) may then be written in the form

$$\vec{N}^{(m)}(r, s) = R\vec{N}^{(m-1)}(r, s) + \delta_{rs}\vec{L}, \tag{21}$$

where R=f-order hypermatrix and $\vec{L}$=f-dimensional hypervector with components determined by equation (15) in which the third order matrix $S(\Omega_1)$ is replaced by the corresponding fifth order matrix $\sum(\Omega_1)$ and the five-dimensional vector $\vec{x}(\Omega_1)$; the components of these latter are quadratic functions of the elements of $S(\Omega_1)$.

Substituting in (21) the equation linking $\vec{N}^{(m-1)}(r, s)$ with $\vec{N}^{(m-2)}(r, s)$ and so on as far as $\vec{N}^{(0)}(r, s)$ which consists of elements in the first column of the diagonal hypermatrix together with the corresponding I_{rr} components, we find

$$\vec{N}^{(m)}(r, s) = R^m[\vec{N}^{(0)}(r, s) - \delta_{rs}\vec{Z}] + \delta_{rs}\vec{Z}, \tag{22}$$

where

$$\vec{Z} = (I - R)^{-1}\vec{L} \tag{23}$$

=a hypervector in which only the components of $(Z)_1$, corresponding to the components of $\vec{e}_t\{N\}_{11}\vec{e}_t$, differ from zero and are equal to 1/3. This follows from the orthogonal character of the $S(\Omega)$ matrices.

The hypervector $\vec{M}^{(m)}(r, s)$ made up of elements of the first row of the hypermatrix $M^{(m)}(r, s)$ is interpolated analogously in accordance with the same principle. The relevant recurrent equation has the form

$$\vec{M}^{(m)}(r, s) = [\vec{M}^{(0)}(r, s) - \delta_{rs}\vec{Z}]R'^{m} + \delta_{rs}\vec{Z}, \tag{24}$$

in which the element of the hypermatrix R' is determined by equation (15) where $S(\Omega_1)$ is replaced by $\tilde{\sum}(\Omega_1)$, a term derived by transposing the $\sum(\Omega_1)$ matrix and by substituting every $s_{uv}(\Omega_1)$ in $s_{ru}(\Omega_1)\cdot\vec{M}^{(0)}(r, s) = \vec{N}^{(0)}(r, s)$.

Taking into account the linear relation between the elements of the matrices $M^{(m)}(r, s)$ and $N^{(m)}(r, s)$ and the components of the corresponding vectors, we substitute equations (22) and (24) in (16) and sum the dual and triple geometrical progressions, the denominators of which are the matrices W, R and R'.

We are confining ourselves to n^2 and n order terms, neglecting terms that do not contain n and also terms containing the matrices W^n, R^n and R'^n, the elements of which are negligibly small.* The latter follows from the physical significance of the elements making up the matrices W, $N(r,s)$ and $M(r,s)$ (cf. e.g. equation (12)). We find:

$$S_{rs}=\frac{9}{10}\frac{nl'^2}{\overline{h}^3}\vec{e}_z\Big\{[-I+2(I-W)^{-1}]/(I-R)^{-1}\vec{N}'(r,s)/+$$

$$+/\vec{N}'(r,s)(I-R')^{-1}/[-I+2(I-W)^{-1}]-/\vec{N}'(r,s)/+$$

$$+2W(I-W)^{-1}I_{rs}W(I-W)^{-1}-\frac{2}{3}\delta_{rs}W^2(I-W)^{-2}\Big\}\vec{e}_z, \tag{25}$$

in which

$$\vec{N}'(r,s)=\vec{N}^{(0)}(r,s)-\delta_{rs}\vec{Z}. \tag{26}$$

I = a unitary matrix and the oblique lines denote the process of transition from vectors $\vec{M}$ and $\vec{N}$ to the corresponding matrices.

Further calculation is reduced to determination of the elements of the hypermatrices $(I-W)^{-1}$, $(I-R)^{-1}$ and $(I-R')^{-1}$: this is possible by regarding these f order hypermatrices as $3f$ and $5f$ order matrices respectively and by determining as a general rule the elements of the reverse matrix to the one given. Even in the case of just two rotation isomers a calculation of this type is an extremely tedious operation. In certain exceptional cases, however, the systems of recurrent equations can be divided into independent sub-systems of lower orders and calculation is greatly simplified.

We shall now consider the application of the present method to calculating the optical anisotropy of isotactic polymers.

CALCULATION OF THE OPTICAL ANISOTROPY OF ISOTACTIC POLYMERS

The conditions of symmetry for isotactic polymers of the type $(-CH_2-CHR-)_n$ that crystallize in the form of a spiral [11] indicate the presence in solution of two rotation isomers in each monomer unit, their energies being equal correct to the correlation of the internal rotations in the adjacent monomer units ("isoenergetic" rotation isomers). Moreover, provided the R-group is sufficiently large there is considerably less energy associated with the rotation isomers of crystalline configuration than with the other rotation isomers thus the latter cannot be considered [9, 11, 13 and 14].

The elements g_{11} and g_{22} of the matrix G (8) in this case are equal and it is possible to write the generalization $g_{11}=g_{22}=1$ without any limitation. The

* The special case discussed in paper [6] is an exception.

hypermatrix W (15) can be written in the form (the ratio of two arbitrary elements of matrix U, viz. U_{11}/U_{21} is written equal to unity):

$$W = \frac{1}{2}\begin{pmatrix} S^{(1)}+S^{(2)} & S^{(1)}-S^{(2)} \\ \frac{\lambda^2}{\lambda_1}(S^{(1)}-S^{(2)}) & \frac{\lambda_2}{\lambda_1}(S^{(1)}+S^{(2)}) \end{pmatrix}, \tag{27}$$

where $S^{(1)}=S(\Omega_1)$ and $S^{(2)}=S(\Omega_2)$ are cosine matrices of the angles corresponding to the two possible configurations of the monomer units; λ_1 and λ_2 ($<\lambda_1$) are characteristic values of the matrix G. The hypermatrices R and R' are composed of matrices $\sum^{(1)}$ and $\sum^{(2)}$ and hence of $\tilde{\sum}'^{(1)}$ and $\tilde{\sum}'^{(2)}$ on the same principle as matrix W is composed of matrices $S^{(1)}$ and $S^{(2)}$.

It has been demonstrated by X-ray diffraction [15, 16] that a large number of isotactic polymers crystallize in the form of 3_1 spirals with three monomer molecules in a single repeat and with a repeat frequency corresponding to a (0·120) or (−120·0) configuration of monomer units. We shall turn our attention to a number of more general cases with a $(0,\varphi)$ and $(-\varphi,0)$ monomer unit configuration.

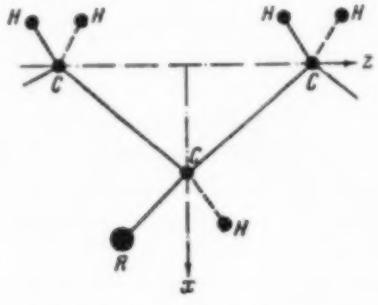

FIG. 1. Interpolation of system of coordinates.

We shall interpolate local systems of coordinates shown in Fig. 1 (cf. also [9]). There the transition matrices $S^{(1)}-S(0,\varphi)$ and $S^{(2)}-S(-\varphi,0)$ differ only by the sign of the elements 12, 13, 21 and 31 (cf. [9]). On reversal of the direction of all X_k axes the matrix $S^{(1)}$ is converted to $S^{(2)}$ and conversely. Since the diagonal elements of the matrix G are coincident and the hypermatrices W, R and R' are related to the elements g_{12} and g_{21} of matrix G only by the root $\lambda_{1,2}=1\pm\sqrt{g_{12}g_{21}}$, it can readily be shown that

$$S_{xy}=S_{xz}=0. \tag{28}$$

Taking into account (5) we find that expression (1) for the mean optical anisotropy of an isotactic polymer will not contain non-diagonal tensor components for the polarizability of the monomer unit.

Substituting $S^{(1)}$ and $S^{(2)}$ in formula (27) we are satisfied that in calculating the 6th and 5th order determinants whereby the elements of the matrix $(I-W)^{-1}$

are expressed, the matrix $(I-W)$ can be reduced to a quasi-diagonal form. Calculation of the elements of $(I-W)^{-1}$ leads to calculation of the third and second order determinants.

The matrices $\sum^{(1)}=\sum(0,\varphi)$ and $\sum^{(2)}=\sum(-\varphi,0)$ which form part of the hypermatrix R, differ only by the sign of certain elements and thus half the elements of the matrix R are converted to zero and the system of 10th order equations (22) falls into two sub-systems of the 5th order, one of which links the components of the vectors $\vec{N}^{(m)}$ and $\vec{N}^{(0)}$, corresponding to matrix elements $\vec{\vec{e}}_y\{N\}_{\alpha 1}\vec{e}_z$; $\vec{\vec{e}}_z\{N\}_{\alpha 1}\vec{e}_z$; $\vec{\vec{e}}_x\{N\}_{\alpha 1}\vec{e}_x$; $\vec{\vec{e}}_x\{N\}_{\beta 1}\vec{e}_z$; $\vec{\vec{e}}_x\{N\}_{\beta 1}\vec{e}_y$ at $\alpha=1$ and $\beta=2$, and the other linking the same elements at $\alpha=2$ and $\beta=1$. Taking into account that $[(I-W)^{-1}]_{13}=[(I-W)^{-1}]_{31}=[(I-W)^{-1}]_{35}=[(I-W)^{-1}]_{53}=[(I-W)^{-1}]_{36}=$ $=[(I-W)^{-1}]_{63}$, we find that expression (25) will contain only the elements present in the first sub-system, the derivation of which may be written in the form:

$$\vec{n}^{(m)}(r,s)=R^{(m)}\vec{n}'(r,s)+\vec{l}\delta_{r,s}\,. \tag{29}$$

where $\vec{n}^{(m)}(r,s)$; $\vec{n}'(r,s)=\vec{n}^{0}(r,s)-\vec{l}\delta_{rs}$ and $\vec{l}$ are five-dimensional vectors

$$\vec{\vec{n}}^{(m)}(r,s)=[\vec{\vec{e}}_y\{N^{(m)}(r,s)\}_{11}\vec{e}_z;\ \vec{\vec{e}}_z\{N^{(m)}(r,s)\}_{11}\vec{e}_z;\ \vec{\vec{e}}_x\{N^{(m)}(r,s)\}_{11}\vec{e}_x;$$

$$\vec{\vec{e}}_x\{N^{(m)}(r,s)\}_{21}\vec{e}_z;\ \vec{\vec{e}}_x\{N^{(m)}(r,s)\}_{21}\vec{e}_y]. \tag{30}$$

$$\vec{\vec{l}}=\left(0,\frac{1}{3};\frac{1}{3};0;0\right) \tag{31}$$

and R is a 5th order matrix

$$M=\begin{pmatrix} s_{12}s_{22}+s_{13}s_{23} & s_{22}s_{22}-s_{23}s_{23} & s_{21}s_{21}-s_{23}s_{23} & s_{21}s_{22}+s_{23}s_{21} & s_{21}s_{23}+s_{22}s_{21} \\ 2s_{12}s_{22} & s^{2}_{22}-s^{2}_{23} & s^{2}_{21}-s^{2}_{23} & 2s_{21}s_{22} & 2s_{21}s_{23} \\ 2s_{13}s_{23} & s^{2}_{23}-s^{2}_{33} & s^{2}_{21}-s^{2}_{33} & 2s_{21}s_{23} & 2s_{21}s_{33} \\ \frac{\lambda_2}{\lambda_1}(s_{12}s_{22}+s_{13}s_{23}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{22}-s_{13}s_{23}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{21}-s_{13}s_{23}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{22}+s_{13}s_{21}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{23}+s_{13}s_{21}) \\ \frac{\lambda_2}{\lambda_1}(s_{12}s_{23}+s_{13}s_{33}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{23}-s_{13}s_{33}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{21}-s_{13}s_{33}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{23}+s_{13}s_{21}) & \frac{\lambda_2}{\lambda_1}(s_{12}s_{33}+s_{13}s_{21}) \end{pmatrix} \tag{32}$$

(s_{uv}= elements of the matrix $S^{(1)}$).

The system of equations (24) for $\vec{\vec{M}}^{(m)}$ analogously falls into two sub-systems and we are interested in the derivation of the one with matrix $\widetilde{R}'$ obtained from R by multiplication of the 4th and 5th columns and division of the 4th and 5th rows by λ_2/λ_1, substitution of $s_{uv}(\Omega)$ for $s_{vu}(\Omega)$ and transposition.

The components of the vectors $(I-R)^{-1}\vec{n}'(r,s)$ can be calculated from the formula

$${}^{n}\Delta_i(r,s)=[(I-R)^{-1}\vec{n}'(r,s)]_i=\frac{\sum_{v=1}^{5}\Delta_{vi}(I-R)\vec{n}'_v(r,s)}{D(I-R)}\,, \tag{33}$$

where the numerator equals the determinant of the matrix $I-R$ in which the column notated i is replaced by the vector $\vec{n}'(r,s)$ and $D(I-R)$ is the determinant of the matrix $I-R$. It can readily be shown that ${}^{m}\Delta_1(r,s)=-(-1)^{r+s}{}^{n}\Delta_1(r,s)$ ${}^{m}\Delta_2(r,s)=(-1)^{r+s}{}^{n}\Delta_2(r,s)$; ${}^{m}\Delta_4(r,s)=(-1)^{r+s}\frac{\lambda_1}{\lambda_2}{}^{n}\Delta_4(r,s)$.

By carrying out the calculation we shall find

$$S_{rr}=\frac{1}{p}S_{rr}^{(1)}+pS_{rr}^{(2)}, \tag{34}$$

where

$$S_{rr}^{(1)}=\frac{3}{20}\frac{7+3\cos\alpha}{\sin^2\alpha}\left|\frac{1}{3}-\delta_{2r}+(\delta_{3r}-\delta_{1r})\cos\alpha\right|, \tag{35}$$

$$S_{rr}^{(2)}=\frac{3}{20}\frac{1}{1+\cos\alpha}\left|1-5\delta_{1r}+2\delta_{2r}-\cos\alpha\left(\frac{1}{3}+\delta_{1r}-2\delta_{2r}\right)\right|+$$

$$+\frac{6}{5}\frac{1}{1+\cos\alpha}\cdot\frac{1}{1-\cos\varphi}\left(\frac{1}{3}-\delta_{1r}\right)+\frac{3}{40}\frac{(1+\cos\alpha)(1-\cos\varphi)}{1+\cos\varphi}\left(\frac{1}{3}-\delta_{2r}\right). \tag{36}$$

where

$$p=\frac{\sqrt{g_{12}g_{21}}}{g_{11}}=\exp\left|-\frac{1}{RT}\left(\frac{U(\Omega^{(1)},\Omega^{(2)})+U(\Omega^{(2)},\Omega^{(1)})}{2}-U(\Omega^{(1)},\Omega^{(1)})\right)\right|. \tag{37}$$

DISCUSSION

If $\pi=\alpha=\pi$ tetrahedral angle and $\varphi=120^\circ$, then $S_{rr}^{(2)}=0$ and

$$S_{rr}=\frac{S_{rr}^{(1)}}{p}. \tag{38}$$

Equality (38) is approximately fulfilled too when $\pi=\alpha$ and φ differ only slightly from $109^\circ 30'$ and 120° respectively; furthermore, the larger $1/p$, the more strictly is (38) fulfilled.

We shall interpolate the optical anisotropy $\Delta\gamma$ of the monomer unit on the axes ξ, η, ζ which correspond to the principal axes of a fully drawn polymer chain. Taking into account that the chain of an isotactic polymer on stretching is a straight spiral (cf. Fig. 2), we have.

$$\Delta\gamma=\alpha_{\zeta\zeta}-\frac{\alpha_{\xi\xi}+\alpha_{\eta\eta}}{2}=\frac{1+3\cos\alpha}{4}\alpha_{zz}-\frac{\alpha_{yy}}{2}+\frac{1-3\cos\alpha}{4}\alpha_{xx}. \tag{39}$$

Substituting (35) in (1), using (39) and making allowance for the fact that all $S_{rs}=0$, at $r\neq s$ we obtain

$$\Delta A=\frac{1}{p}\frac{7+3\cos\alpha}{5\sin^2\alpha}\Delta\gamma. \tag{40}$$

Accordingly the mean anisotropy associated with the polarizability of a macromolecule is expressed by the anisotropy of a monomer unit in the axes of a spiral. This is understandable because where there is a correlation between the configurations of monomer units, the adjacent units tend to acquire the same configuration and so the polymer chain contains regular spiral segments of varying lengths. Their length is governed by the quantity $1/p$, their anisotropy is $\sim\Delta/p$, thus also $\Delta A \sim \Delta\gamma/p$.

As pointed out above we find that $\Delta\gamma$ is independent of the monomer unit configuration. Fulfilment of this condition for the CHR group necessitates axial symmetry of the side-chain with respect to the C — R bond or that the

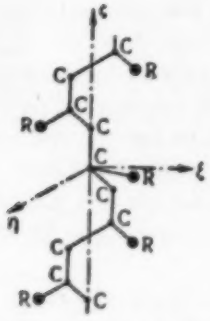

FIG. 2. Isotactic 3_1 spiral.

rotation in the side-chain be independent of that in the main valence chain. Although the CH_2 groups are not fixed in local systems of coordinates their contribution to $\Delta\gamma$ is almost independent of the configuration of the monomer units. Consequently if the valence angles in the methylene groups were tetrahedral, it would be possible, according to Sack [17],* to deduct the isotropic tensor of the polarizability of the CH_4 group from the $-CH_2$ tensor and as a result the polarizabilities of the C — H bonds would be deducted from the polarizabilities of the C — C bonds. In the case of non-tetrahedral valence angles this method is approximately correct because the anisotropy of the C — H bonds is small. For strongly anisotropic polymers the C — H bonds may generally be regarded as isotropic.

The only isotactic polymer whose mean optical anisotropy is known is polystyrene [18] the molecules of which have the form of a 3_1 spiral in the crystalline state. Yet the rotation of the benzene rings in polystyrene may be determined by the rotation in the main valence chain and for comparison with experiment corresponding theories need to be developed. If this relationship is assumed to be absent expression (40) may be used for polystyrene, $\Delta\gamma$ being a function of the rotation in the benzene ring, viz. a function of $\sin^2\psi$, where ψ is the angle

* Translator's note. Sack is cited against [3] in the references.

of deviation of the benzene ring from the plane passing through the C — H and C — C_6H_5 bonds. The correlation factor p in expression (40) may be calculated comparing the theoretical and experimental findings on the dimensions of isotactic polystyrene [9]. In paper [9] it was found that $p=0{\cdot}35$ and correspondingly $(U_{12}+U_{21}/2)-U_{11}=600$ cal/mol. Assuming $\pi-\alpha=116°30'$ and $\varphi=120°$ [15, 16] and using values of the C — C and C — H bond anisotropy $\Delta\alpha_{CC}=18{\cdot}6\times10^{-25}$ cm^3, $\Delta d_{CH}=2{\cdot}1\times10^{-25}$ cm^3, and of the benzene ring $\alpha_1-\alpha_2=59{\cdot}6\times10^{-25}$ cm^3 [12, 19], we find by substituting the calculated value of $\Delta\gamma$ in formula (40) that theory accords with the experimental value $\Delta A=-140\times10^{-25}$ cm^3 [18] for $\sin^2\psi\simeq0$. This is nearly tantamount to the complete absence of rotation in the benzene rings.

It is more natural to apply the present theory to polymers whose side-chains have axial symmetry with respect to the C — R bonds; such a polymer is polypropylene, although relevant experimental findings are lacking. Assuming the p factor of polypropylene to be approximately the same as that of polystyrene (in keeping with their close dimensions) and using the values $\pi-\alpha=114°30'$, $\varphi=120°$ [15, 16], we find $\Delta A\sim30\times10^{-25}$ cm^3.

In conclusion the author acknowledges his grateful thanks to M. V. Vol'kenshtein and Iu. Ia. Gotlib for their interest in this paper.

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CONCLUSIONS

(1) The optical anisotropy of stereospecific polymers in the polyvinyl series with axially symmetrical side-chains can be calculated in rotation-isomer approximation, allowance being made for all the basic interactions in the chain by means of a modified form of Izing's matrix method.

(2) In the case of isostatic polymers crystallizing in the form of 3_1 spirals, the problem is reduced to calculation of the fifth order determinants.

(3) The optical anisotropy of an isotactic polymer is proportional to the optical anisotropy of the monomer unit in the axes of the 3_1 spiral and to the mean number of successive monomer units located in the same configurations.

Translated by G. CAMERON

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STEREOSPECIFICITY OF POLYMERS AS A FUNCTION OF THE CONDITIONS OF POLYMERIZATION*

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(*Received* 27 *March* 1959)

INTRODUCTION

THE tremendous scientific and technical importance of vinyl polymers with a stereoregular structure has in recent years aroused considerable interest in the stereo-chemical structure of macromolecules. Natta's papers [cf. e.g. 1–4] report the preparation of a large number of isotactic vinyl polymers and syndiotactic poly-1,2-butadienes by heterogenous catalysis. Recently [5] stereospecific (apparently syndiotactic [6] polymethyl methacrylate was obtained by Fox *et al.* who also used free-radical polymerization at low temperature; the stereospecificity of the resulting polymer is inversely proportional to the polymerization temperature [7]. Syndiotactic polymethyl methacrylate can further be synthesized by homogeneous catalytic polymerization at low temperature in a strongly solvating medium [5, 8]; as the solvating power of the medium diminishes anisotactic polymer is formed [5, 8].

These experimental facts point to the existence of two mechanisms which are responsible for the stereospecificity of the polymerization: the influence of the end of the growing chain which produces a predominantly syndiotactic structure [7], and the influence of the catalyst which, as a rule, yields a chiefly isotactic structure. The former mechanism, the effectiveness of which rapidly increases in inverse proportion to the polymerization temperature, is determinable provided (a) there is no catalyst (free-radical polymerization) or (b) the catalyst has no stereospecific action (homogeneous catalytic polymerization in a strongly solvating medium). As the polymerization temperature rises the influence of this mechanism declines to the point where the polymers obtained in the absence of a stereospecific catalyst are amorphous. For polymethyl methacrylate the "transition" temperature is in the region of 0°C; polyvinylchloride, however, prepared by free-radical polymerization at room temperature retains its crystallizability and its characteristic frequency reveals a syndiotactic structure [9].

* Vysokomol. soedin. **1**: No. 6, 846–851, 1959.

CORRELATION BETWEEN THE CONSECUTIVE ADDITIONS OF MONOMER UNITS AND THE FORMATION MECHANISM OF STEREOBLOCK POLYMERS

The stereospecific influence of the end of the growing chain (the likelihood of such an influence existing was first referred to by Huggins [10]) is governed by the differences in the transition state energies corresponding to isotactic and syndiotactic addition. Goode [7] asserts that this difference is associated with the fact that when a monomer is added to the end of the growing chain the CHR-group which terminated the chain before the addition may assume an isotactic or syndiotactic arrangement with respect to the preceding CHR-group. The difference between the transition state energies (i. e. the difference in the activation energies) amounts to the difference in the energies of these two arrangements of the CHR-groups. Schulz [11] has put forward the view that syndiotactic addition is energetically more economical; this was recently borne out by Fordham's model calculation.

The physical cause behind the dependence of the chain energy on the isotactic or syndiotactic arrangement of the CHR-group is the van der Waals interaction between chemically unrelated atoms and groups which is also responsible for retarding the internal rotation in the chain. The authors and Gotlib have formulated a theory to explain the influence of the retardation of internal rotation on the properties of macromolecules in solution which is based on Vol'kenshtein's rotary-isomeric chain model [12] and on the method of determining the rotary isomers of monomer units proposed by one of us together with Sharonov [13]. Comparison of this theory with experimental findings reveals the presence of a definite interaction both between adjacent CR_2 or CHR-groups in polymers of the $(-CH_2-CR_2-)_n$ and $(-CH_2-CHR-)_n$ type, and between the nearest non-adjacent CR_2 or CHR-groups (separated by four members of the principal chain) [14–16]. Thus, for isotactic polystyrene the difference in energy between non-identical and identical spiral configurations of adjacent monomer units governed by the interaction of the nearest, non-adjacent phenyl groups amounts to about 600 cal/mol [14]. These interactions enlarge the chains in solutions but so far as is known cannot be responsible for their rigid spiral configuration in the dissolved state. The opposite view [17] based on an analogy with polymers which form incomparably stronger intermolecular hydrogen bonds we regard as inconclusive.

The occurrence of a definite interaction between the non-adjacent CHR-groups must produce a state where the probability of isotactic or syndiotactic monomer addition is governed by the manner in which the preceding monomer was added. Consequently, notwithstanding the opinion held by Coleman [18], this relationship can also be operative even in the absence of a catalyst.

Thus we must be confronted not with two probabilities α_i and α_s, but with four; α_{ii}, α_{is}, α_{si} and α_{ss} (α_{is}—probability of syndiotactic addition of the nth

monomer unit to the $(n-1)$th provided the $(n-1)$th unit has been added isotactically to the $(n-2)$th and so forth) related by the obvious conditions:

$$\alpha_{ii}+\alpha_{is}=1, \qquad \alpha_{si}+\alpha_{ss}=1 \tag{1}$$

and forming a Markoff series. When considered in this way the formation of stereoisomeric polymers is formally identical with copolymerization [19]. The presence of four probabilities of addition in copolymerization is governed by the different chemical nature of the two types of monomer unit. The correlations between the successive additions of monomer units can normally be disregarded here [19] as follows from the fact that the steric effects associated with this type of correlation are generally slight compared with the effects arising from the different reactivities of the monomers. However, in the formation of stereoisometric polymers the difference in reaction rates is attributable exclusively to steric effects.

Where there are four probabilities of addition α_{pq} we obtain for the proportion of monomer units contained in an isotactic sequence consisting of more than N units the expression:

$$f_N=\sum_{n=N+1}^{\infty} n\,(1-\alpha_i)\,\alpha_{si}\alpha_{ii}^{n-1}\,(1-\alpha_{ii})=\alpha_i\,\alpha_{ii}^{N}\,(1+N\alpha_{is}). \tag{2}$$

where $\alpha_i=\alpha_i\,\alpha_{ii}+\alpha_s\,\alpha_{si}=$ an *a priori* probability of isotactic addition. If α_{pq} is not dependent on the first term equation (2) becomes

$$f_N=\alpha_i^{N+1}\,(1+N\alpha_s). \tag{3}$$

obtained in paper [7]. Expressions for the proportion of the monomer units contained in sindiotactic sequences can be derived from equation (2) and (3) by transposing the i and s indices.

The theory as to the presence of a correlation between the successive additions of monomer units to the end of the growing chain readily accounts for the existence of crystalline stereoblock polymers, the chains of which consist of alternating isotactic and sindiotactic sequences. Polymers of this type were prepared by the homogeneous catalytic polymerization of methyl methacrylate in a moderately solvating medium at low temperature [7]. It will be clear that the existence of such polymers cannot be explained in terms of the two probabilities α_i and α_s (which are independent of time). In point of fact the occurrence of long isotactic and syndiotactic sequences needed to form crystallites of both types necessitates that α_i and α_s should be close to unity simultaneously, and this conflicts with the obvious condition $\alpha_i+\alpha_s=1$. Against this in the case considered above involving four probabilities α_{ii} and α_{ss} can be as close to unity simultaneously as possible without infringing condition (1).

As pointed out earlier the interaction of the adjacent CHR-groups appears to result preferentially in sindiotactic addition, viz. it increases α_{is} relative to α_{ii}, and α_{ss} relative to α_{si}. We shall assume that the interaction of the nearest,

non-adjacent CHR-groups stabilizes an addition analogous to the preceding one, i.e. increases α_{ii} and α_{ss} (cf. [17]). When the difference between α_{ii} and α_{is} resulting from these interactions becomes smaller, that between α_{si} and α_{ss} grows, and when α_{ii} and α_{is} are similar, $\alpha_{ss} \gg \alpha_{si}$. Furthermore a syndiotactic polymer is obtained.

The catalytic effect which increases α_{ii} and α_{si} may lead to the simultaneous fulfilment of $\alpha_{ii} \gg \alpha_{is}$ and $\alpha_{ss} \gg \alpha_{si}$ which are indispensable conditions for the formation of a stereoblock polymer (even where the influence of the catalyst is independent of the preceding addition). With increasing stereospecificity of the catalytic influence (owing, say, to a falling-off in the solvating power of the medium) the condition $\alpha_{ss} \gg \alpha_{si}$ will cease to be fulfilled and an isotactic polymer will result. On the other hand if there are just two probabilities α_i and σ_s such that $\alpha_s \gg \alpha_i$ in the absence of catalyst, as the stereospecificity of the catalyst grows we shall first find $\alpha_i \approx \alpha_s$ (atactic polymer) and then $\alpha_i \gg \alpha_s$ (isotactic polymer).

THE PROPERTIES OF MACROMOLECULES IN SOLUTION AS A METHOD TO STUDY THE STEREOCHEMICAL STRUCTURE ("MICROTACTICITY") OF THE CHAIN

In order to study quantitatively the influence of the polymerization conditions (temperature, medium, catalyst used and so forth) on the stereochemical structure of the chains we need to have at our disposal methods with which to determine the stereochemical structure from the properties of the polymers obtained. The X-ray method commonly employed for this purpose has its limitations in that the crystallinity of the polymers rapidly drops to zero with decreasing stereospecificity (it follows from equations (2) and (3) that the proportion of monomer units contained in long sequences is practically zero if α_i and α_s differ noticeably from unity).

Any quantitative method to determine the relationship between the stereochemical structure of the macromolecules and the polymerization conditions for atactic polymers, as they are called (with α_i ranging from 0·1 to 0·9) must be based on physical properties that to a large extent are independent of the regularity of the stereochemical chain structure (e.g. the crystallinity) but which are directly governed by the probabilities of isotactic and syndiotactic additions of monomer ("microtacticity" of the chain). The physical properties that have occasionally been used for this purpose such as solubility, degree of swelling, vitrification temperature etc. are unsuitable for the quantitative evaluation of α_i because at present there is no theory linking them with the structure of the chain. So far as is known the above applies to the infra-red spectra of stereoisomeric polymers in non-polarized light because considerable difficulty is encountered in working out the relationship between the frequency, and especially the intensity, of the absorption bands of the polymer chain and its stereochemical structure [20].

As demonstrated by the authors in 1954 [21, 22] the physical properties of macromolecules in solution (dimensions and dipole moments) must be related to the stereochemical structure of the chains. This conclusion, which was also extended by Gotlib [24] to the optical anisotropy of macromolecules, was subsequently confirmed by one of us in collaboration with Sharonov [23] allowing for the correlation between the rotations about adjacent segments. A series of papers have compared the dimensions of molecules of isotactic and atactic polystyrene [25–29] and polypropylene [30–33] determined from the intrinsic viscosity [25, 27–33] and from light-scattering [26, 29, 32]: in both cases the dimensions of the isotactic and atactic polymer molecules proved identical. In a number of cases, however, (cf. e.g. [27]), at a given molecular weight, the second virial coefficient of the isotactic polymer is much lower than of the atactic polymer. This led Krigbaum, Carpenter and Newman [29] to assume that at a given molecular weight the "undisturbed" dimensions of isotastic polystyrene molecules (measurable at the θ-point) must be larger than the dimensions of atactic polystyrene molecules. (According to this theory, in good solvents the increase in the "undisturbed" dimensions is offset by the reduced influence of the space effects). Unfortunately all attempts so far to measure the properties of isotactic macromolecules at the θ-point have been unsuccesful [29].

The difficulties involved in measuring the dimensions of isotactic polymers in θ-solvents make it particularly desirable to obtain experimental proof of the theories [22–24] which relate the dipole moments and the optical anisotropy of the macromolecules to their stereochemical structure because these properties are practically insensitive to the nature of the solvent. Such proof was recently adduced by Tsvetkov and Magarik [34] who showed that the optical anisotropy of an isotactic polystyrene macromolecule in solution is greater than that of the normal atactic polymer by a factor of about 1·5. Moreover they were the first to confirm experimentally the relationship of macromolecules in solution to their stereochemical structure.

Accordingly the properties of macromolecules in solution can be used for the quantitative determination of chain microtacticity. The findings reported in paper [34] attest that the stereochemical structure of polystyrene is by no means isotactic (cf. [22]). Pre-requisites for a more accurate determination of the microtacticity are a knowledge of the optical anisotropy of sindiotactic polystyrene and the development of a theory to account for the physical properties of the atactic molecules in solution. At the same time the occurrence of a retarding effect in respect of the internal rotation may lead to a non-linear relation between the properties of the isotactic and syndiotactic polymers (a theory dealing with the analogous non-linear relation for copolymers is formulated in paper [35]). Information on the microtacticity of chains can also be gained by studying their infra-red dichroism [20] and (in particular cases) by studying the kinetics of certain reactions within the chains [36].

One of the problems whose solution requires a knowledge of the microtacticity of the chain is the experimental study of the relationship between the probability of stereospecific addition of the monomer unit to the end of the growing chain and the degree of crystallinity of the polymer (cf. equations (2) and (3)). Block copolymers composed of isotactic and atactic sequences and having various degrees of crystallinity are suitable material for solving this problem [37, 38].

CONCLUSIONS

(1) The interaction between nearest, non-adjacent R-groups in $(-CH_2-CHR-)_n$ type polymers must result in a correlation between the successive additions of monomer units.

(2) The existence of such a correlation accounts for the phenomenon of stereoblock macromolecules consisting of alternate isotactic and sindiotactic sequences and formed by homogeneous polymerization in a moderately solvating medium where the stereospecific influence of both the catalyst and the end of the growing chain is substantial.

(3) The properties of polymers in solution can serve as a method to examine the microtacticity of macromolecules.

Translated by G. CAMERON

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THE KINETICS OF INDUCED POLYMERIZATION*

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(*Received* 15 *April* 1959)

INITIATORS are extensively used to accelerate a host of chain processes in industry and in research. Thus the oxides of nitrogen serve as initiators in the gaseous phase oxidation of methane to produce formaldehyde and further in the oxidation of numerous other hydrocarbons. A variety of initiators exists, e.g. organic peroxides, hydroperoxides, azo-compounds, multivalent ions and such like.

Induced chain processes have certain kinetic characteristics and it is the aim of the present paper to examine them in terms of the simplest chain mechanism.

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1. THE KINETICS OF AN INDUCED CHAIN REACTION

In an unbranched chain reaction the conversion rate (w) is a function of the rate at which active centres are formed. Consequently the addition of substances (initiators) capable of generating active centres at a faster rate than that of the starting product and thus capable of raising the concentration of active centres in the reaction system, enhances w. Nevertheless as the concentration of active centres [R·] grows their rate of recombination accelerates and the proportion of wastefully consumed initiator rises with the possible result of a depressed yield of the finished product from the chain reaction. This circumstance determines the character of an induced chain conversion process.

Consider the simplest scheme of an unbranched chain reaction in the presence of an initiator:

$$I \xrightarrow{k_1} \mathrm{R}\cdot \quad \text{(initiation)}$$

$$\mathrm{R}\cdot + M \xrightarrow{k} \mathrm{B} + \mathrm{R}\cdot \quad \text{(propagation)}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_p} \quad \text{(rupture)}$$

where I, M and B are molecules of the initiator, of the starting substance and of the final product, and correspondingly k_1, k and k_p are the rate constants of the relevant elementary reactions.

* Vysokomol. soedin. 1: No. 6, 869–877, 1959.

Assuming for simplicity's sake that I undergoes monomolecular decomposition we shall find

$$[I]=[I]_0 e^{-k_d t}, \tag{1}$$

where $[I]_0$ is the concentration of I at the outset ($t=0$).

When the rate of the process is steady $k_0[I]=k_p[R\cdot]^2$, which, taking (1) into account, will give

$$[R\cdot]=(k_0[I]_0/k_p)^{1/2}\exp\{-k_0 t/2\} \tag{2}$$

The conversion rate $M\rightarrow B$ is equal to

$$w=-\frac{d[M]}{dt}=k[R\cdot][M]. \tag{3}$$

Substituting (2) in (3) we shall find

$$w=k\sqrt{\frac{k_0[I]_0}{k_p}}[M]e^{-\frac{k_0}{2}t}. \tag{4}$$

Integrating (4) with $[M]=[M]_0$, $t=0$ will yield

$$[M]=[M_0]\exp[-\alpha/k_0(1-e^{-\frac{k_0}{2}t})], \tag{5}$$

where $\alpha=2k\sqrt{k_0[I]_0/k_p}$. The degree of conversion θ which is equal to $\frac{[M_0]-[M]}{[M_0]}$ can be represented by the expression

$$\theta=1-\exp\left[-\frac{\alpha}{k_0}(1-e^{-\frac{k_0}{2}t})\right]. \tag{6}$$

At low values of θ expression (6) can be simplified using the approximation:

$$\exp[-\alpha/k_0(1-e^{-\frac{k_0}{2}t})]=1-\alpha/k_0(1-e^{-\frac{k_0}{2}t}); \tag{7}$$

and then, by substituting $\alpha=2k\sqrt{k_0[I]_0/k_p}$ and (7) in (6), we shall obtain

$$\theta=\frac{2k\sqrt{[I]_0}}{\sqrt{k_0}k_p}(1-e^{-\frac{k_0}{2}t}).* \tag{8}$$

The rate of conversion $\rho=d\theta/dt$ is equal to

$$\rho=\frac{k\sqrt{k_0[I]_0}}{\sqrt{k_p}}e^{-\frac{k_0}{2}t}. \tag{9}$$

The initial rate is

$$\rho_0=\frac{k\sqrt{k_0[I]_0}}{\sqrt{k_p}} \tag{10}$$

*After this paper had been sent to press the author learned that an equation similar to equation (8) is given (without conclusion) in a short communication by A. V. Tobolsky, J. Amer. Chem. Soc. **80**: 5927, 1958.

and it will obviously be higher the faster the initiator generates active centres (the larger k_0).

The ultimate conversion rate

$$\theta_k = \frac{2k\sqrt{[I]_0}}{\sqrt{k_0 k_p}}, \tag{11}$$

on the other hand will be inversly proportional to k_0.

It follows that the use of initiators with a very high value of k_0 may give rise to the situation where θ_k will be so small as to be undetectable in practice and the behaviour of the reaction in the presence of an initiator will be practically indistinguishable from that of the reaction out of contact with an initiator. The failure of attempts to induce reactions with overreactive substances is clearly attributable to this factor. By way of an illustration we induced the chain oxidation of CH_4+O_2 mixtures at 500°C under static conditions by additions of 1% O_3 which, under these conditions, almost entirely decomposes to form radicals of O: in $\tau=1$ sec. Since under static conditions there was an initial error of about 2 sec in the time readings we found that in the presence of added O_3 the reaction proceeds at practically the same rate as the uninitiated reaction. Analogous results are obtained under continuous conditions for the thermal decomposition (1200°C) of CH_4 initiated by the addition of azomethane. An accelerating action of the initiator was observed only at very low contact times (about 10^{-3} sec).

2. THE KINETICS OF INITIATED POLYMERIZATION

The polymerization reaction is an extremely characteristic example of unbranched chain processes.

We shall use the above formulae to analyze the initiation kinetics of the polymerization process which generally proceeds as follows:

$$\begin{aligned}
&I \rightarrow R_0^{\cdot}\ k_0 && \text{(initiation)}\\
&R_0^{\cdot} + M \rightarrow R_1^{\cdot} \\
&R_1^{\cdot} + M \rightarrow R_2^{\cdot} && \gamma_1 \quad \text{(propagation)}\\
&\cdots\cdots \\
&R_i^{\cdot} + M \rightarrow R_{i+1}^{\cdot} && \gamma_i\\
&R_i^{\cdot} + R_j^{\cdot} \rightarrow && \text{(rupture)}\ k_{ij}.
\end{aligned}$$

where: k_0, γ_i and k_{ij} are the rate constants of the corresponding elementary reactions.

Undre static conditions the polymerization rate will be determined by the expression

$$w = \sum_i \gamma_i [R_i][M].$$

The concentration of radicals ($\sum_i R_i$) will be determined by the equilibrium between the rates of formation and recombination:

$$k_d[I] - \sum_i \sum_j k_{ij}[R_i][R_j].$$

To simlify matters we shall not distinguish between the reactivities of the radicals $R_0^{\cdot}$, $R_i^{\cdot}$, viz. we shall put $\gamma_i = k$. Moreover we shall assume that k_{ij} is equal and identical to k_p which is approximately true for the initial polymerization stage.

With these assumptions:

$$w = k[R^{\cdot}][M] \text{ and } k_d[I] = k_p[R^{\cdot}]^2,$$

where

$$[R^{\cdot}] = \sum_i [R_i^{\cdot}].$$

The conversion of the monomer can then be expressed by the simplified scheme:

$$I \xrightarrow{k_d} R^{\cdot} \quad \text{(initiation)} \tag{1}$$

$$R^{\cdot} + M \xrightarrow{k} R^{\cdot} \quad \text{(propagation)} \tag{2}$$

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_r} \quad \text{(rupture)} \tag{3}$$

and hence the formulae derived in section 1 will be valid for the rate of polymerization and degree of conversion.

Using expressions (10) and (11) we shall analyze the results obtained by Imoto and co-workers [1, 2] for the polymerization of styrene and vinyl chloride initiated by a mixture of benzoyl peroxide (P) and dimethyl aniline (DMA). The initiating reaction in this case is a bimolecular interaction (3):

$$P + DMA \xrightarrow{k_0} R^{\cdot}$$

In accordance with the general scheme (1)–(3), the quantity $k_0 = k_0/[DMA]$.

As shown in Imoto's experiments [1] the quantity $[DMA]$ can be assumed practically independent of time: the integration of equation (4) is thus perfectly valid and the decomposition of benzoyl peroxide to form $R^{\cdot}$ can be considered as proceeding by a monomolecular mechanism at a constant rate k_0, the value of which is $k_0 = k_0[DMA]$.

(a) *Polymerization rate.* In conformity with the experimental conditions defined by Imoto's expression (10) can be written as under:

$$P_0 = \frac{k\sqrt{k_0[DMA][P_0]}}{\sqrt{k_r}}, \tag{10'}$$

viz. at constant starting concentrations of initiator the initial rate of polymerization is proportional to the square root of the activator concentration.

Fig. 1 a and b which have been compiled from Imoto's results for the block polymerization of styrene [1] and for the polymerization of vinyl chloride in tetrahydrofuran [2] reveal that the relation (10′) is satisfactorily fulfilled.

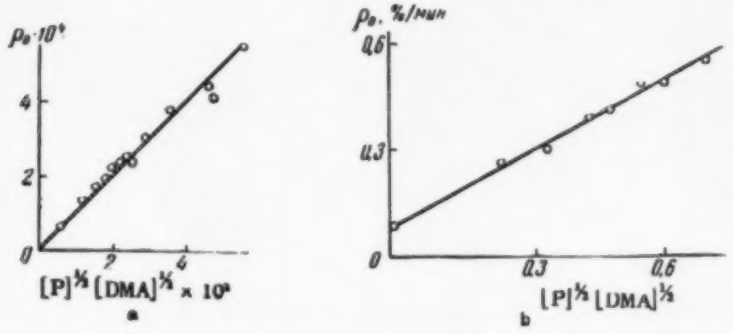

FIG. 1. Initial polymerization rate as a function of the concentration of benzoyl peroxide and dimethyl aniline at 50°C: (a) styrene in mass, (b) vinyl chloride in tetrahydrofuran.

Note that the angular coefficient (A) of the plotted curves is equal to:

$$A = \frac{k\sqrt{k_s}}{\sqrt{k_r}}.$$

(b) *Polymer yield.* For polymerization initiated with an aminoperoxide system we shall write (11) as under:

$$\theta_k = 2k\sqrt{[P_0]}/\sqrt{k_s[DMA]k_r}. \tag{11'}$$

θ_k is plotted as a function of $\sqrt{[P]}/\sqrt{[DMA]}$ in Fig. 2 a and b (based on Imoto's results [1])

The angular coefficient B of the plotted linear curves is:

$$B = \frac{2k}{\sqrt{k_s k_r}}.$$

It will readily be seen that the ratio of the angular coefficients B/A is:

$$\frac{B}{A} = \frac{2}{k_s}.$$

From this k_s can be calculated for styrene

$$A = 1{\cdot}15 \times 10^{-3};\ B = 0{\cdot}125$$

hence

$$k_s = 1{\cdot}8 \times 10^{-2}\ l/\text{mol sec}.$$

We shall compare the calculated value of k_s with the experimental value which can be determined from the experiments [1] on the decomposition of benzoyl peroxide in the presence of dimethyl aniline at the same temperature.

The experimental value of k_s is $1{\cdot}31 \times 10^{-2}$ l/mol/sec.

(c) *Degree of polymerization.* The mean degree of polymerization P is equal to the ratio of the amount of monomer polymerized in time t to the number N

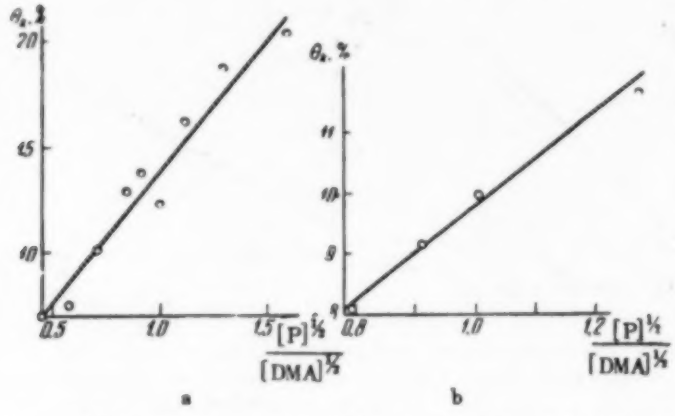

FIG. 2. Ultimate degree of conversion as a function of the benzoyl peroxide and dimethyl aniline concentration at 50°C: (a) styrene in mass, (b) vinyl chloride in tetrahydrofuran.

of polymer molecules formed. In the case of radical disproportionation, $N = \Delta P$. Here

$$P = \frac{\theta[M_0]}{\Delta P}, \tag{12}$$

where ΔP is the amount of initiator (peroxide) decomposed in time t.

From (1) (cf. section 1) it follows that:

$$\Delta P = [P_0](1 - e^{-k_s[DMA]t}). \tag{13}$$

We shall rewrite (8) in the form

$$\theta = \frac{2k\sqrt{[P_0]}}{\sqrt{k_s}[DMA]k_r}\left(1 - e^{-\frac{k_s[DMA]}{2}t}\right). \tag{8'}$$

Substituting (8′) and (13) in (12) we shall obtain

$$P = \frac{2k[M_0]}{\sqrt{k_s}[DMA]k_r[P_0]} \cdot \frac{\left(1 - e^{-\frac{k_s[DMA]t}{2}}\right)}{(1 - e^{-k_s[DMA]t})}. \tag{12'}$$

We shall obtain the expression for the initial degree of polymerization P_0 from (12′) by expanding into a series the exponents in the numerator and denominator:

$$P_0 = \frac{k[M_0]}{\sqrt{k_s}[DMA][P_0]k_r}. \tag{12''}$$

It will readily be realized that at sufficiently high values of t (12) becomes

$$P_k = \frac{2k[M_0]}{\sqrt{k_s}[DMA][P_0]k_r} . \qquad (12''')$$

Comparison of (12″) and (12‴) gives

$$P_k = 2P_0 . \qquad (14)$$

Fig. 3 gives a plot of P_0 versus $[DMA]$ for styrene (based on Imoto's findings [1]). Unfortunately from the account describing the experimental procedure no conclusions can be drawn as to the precision with which P was determined in Imoto's experiments.

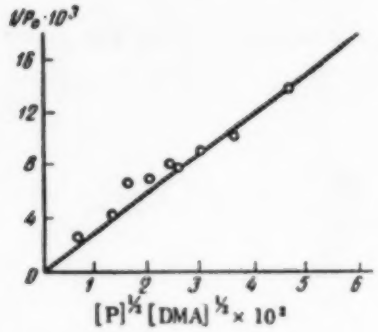

FIG. 3. Initial degree of polymerization rate as a function of the benzoyl peroxide and dimethyl aniline concentration at 50°C.

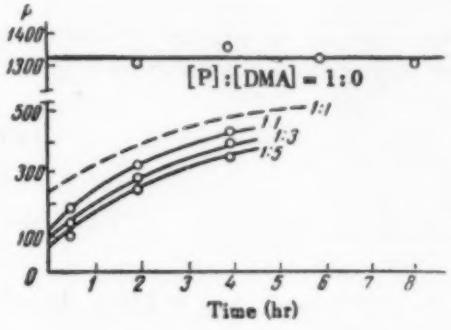

FIG. 4. Degree of block polymerization of styrene as a function of the conversion time at 50°C. The ratio of the initiator concentration to the activator concentration is marked against the curves. The broken line represents a theoretical curve.

P_0 can also be calculated roughly by the following method. Since

$$B = 2k/\sqrt{k_s k_r} ,$$

by substituting (15) in (12″) we shall find

$$P_0 = \frac{BM_0}{2} \cdot \frac{1}{\sqrt{[DMA][P_0]}} . \qquad (16)$$

The values of P_0 calculated from (16) are set out in the Table ($[M]_0 = 8{\cdot}7$ mol/l., $B = 0{\cdot}125$).

P_0 plotted against t (12′) will only give a qualitative-experimental curve (Fig. 4) evidently attributable to simplification of the polymerization mechanism.

(d) *Calculation of chain transfer to the monomer.* In the calculations quoted above we omitted to allow for the eventuality of a chain transfer to the monomer.

The calculation of this reaction will clearly not modify the expression for the monomer conversion rate because the transfer process is not conducive to radical disintegration although it slows down the rate of polymerization.

The rate of polymerization to time t is equivalent to the ratio of the amount of polymerized monomer to the number of polymer molecules formed. The first of these quantities is

$$\int_0^t k[\mathrm{R}^\cdot][M]\,dt\,,$$

the second

$$\int_0^t (k_p[\mathrm{R}^\cdot]^2 + k_{ct}[\mathrm{R}^\cdot][M])dt\,,$$

where kc_t = rate constant of chain transfer to the monomer. Here the degree of polymerization is given by

$$P = \frac{\int_0^t k[\mathrm{R}][M]dt}{\int_0^t k_r[\mathrm{R}]^2 dt + \int_0^t k_{ct}[\mathrm{R}][M]\,dt}\,.$$

In this case, if $k_{ct} \ll k_r[\mathrm{R}]/[M] = \sqrt{k_0 k_r/[M]}$,

$$P = \frac{\int_0^t k[\mathrm{R}][M]\,dt}{\int_0^t k[\mathrm{R}]^2\,dt} = \frac{\theta[M_0]}{\Delta[P]}. \tag{18}$$

and all the relationships mentioned earlier (cf. 12) are correct.

Assuming $k_{ct} = \dfrac{k_r R}{M}$, we have

$$P = \frac{\int_0^t k[\mathrm{R}][M]\,dt}{\int_0^t k_{ct}[\mathrm{R}][M]\,dt} = \frac{k}{k_{ct}}. \tag{20}$$

and consequently, the degree of polymerization in this case is independent of all parameters save the temperature. On this basis the experimental results [1] obtained for the block polymerization of styrene at 50°C (cf. Fig. 4) become understandable. In the presence of DMA, when k_0 is sufficiently large (because $k_0 = k_s\,[DMA]$) to satisfy condition (17), P follows equation (18) and is thus

an increasing function of the conversion time. In the absence of DMA, when k_0 is small and fulfils condition (19), P follows equation (20) and, consequently, remains steady during the polymerization process.

TABLE 1. ORIGINAL DEGREE OF POLYMERIZATION ([P] = $2{\cdot}06 \times 10^{-3}$ MOL/L.)

[DMA] $\times 10^2$ (mol/l.)	0·41	0·82	1·23	2·04	2·86	3·26	4·12	6·18	10·30
Po Found	400	250	180	145	125	130	110	100	75
Po Calculated	575	400	330	250	218	203	180	148	115

3. PRACTICAL CONSIDERATIONS

The dependence of the initial polymerization rate ρ_0 and the degree of polymerization θ on the rate constant k_0 of the decomposition of the initiator can act as a guide in the matter of choosing a suitable initiator. Normally the quality of an initiator is identified with its capacity to generate active centres, i.e. with its k_0 value. However, as stated above, too high a value of k_0 results in a decrease of θ. By developing (6) to the limit $t \to \infty$ it is possible to derive the limit degree of conversion:

$$\theta_\infty = 1 - e^{-\frac{2k\sqrt{[I_0]}}{\sqrt{k_0 k_r}}}. \tag{6'}$$

It follows from (6') that the initiator will be "good" (i. e. $\theta \simeq 1$) only under the condition

$$2k\sqrt{[I_0]}/\sqrt{k_0 k_r} > 1,$$

or

$$k_0 < 4k^2[I_0]/k_r, \tag{21}$$

viz. on condition that it is sufficiently stabilized.

Whilst k_0 satisfies condition (21), a change to less stable initiators (or a larger addition of activator) will increase ρ, practically without affecting $\theta \simeq 1$ and at the same time when

$$k_0 > 4k^2[I_0]/k_r$$

an increase of k_0 will lead to an increase of ρ and to a noticeable decrease in θ_∞.

The path of the kinetic curves for a series of k_0 values is illustrated qualitatively in Fig. 5.

Condition (21) indicates a practical way of increasing the efficiency of an initiator. The recombination constant k_r is proportional to the mobility of the radicals and hence inversely proportional to the viscosity of the medium whereas the propagation constant k is independent of R·. Thus

an increase in the viscosity of the reaction medium by some means results in an increase on the right-hand side of the inequality (21) and this makes it possible to utilize initiators with the largest k_0 values (i.e. to conduct polymerization at faster rates without decreasing θ_∞). The viscosity of the medium can be increased, say, by additions of the polymer itself or of inert, gel-like agents. A further way consists in increasing the pressure.

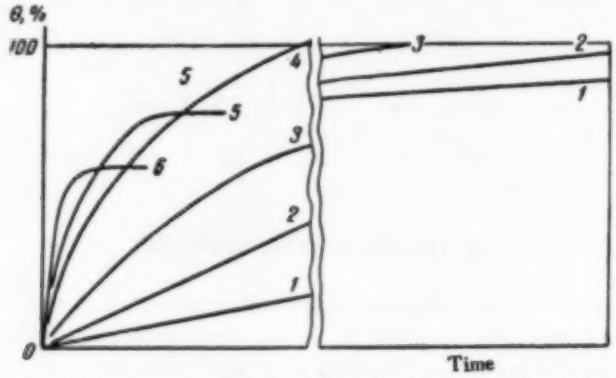

FIG. 5. Kinetic curves at a series of k_0 values (in ascending order of the values from curve 1 to curve 6). (1) (2) (3) (4) k_0 satisfy condition (21); (5) and (6) k_0 do not satisfy this condition.

In conclusion it must be noted that all the results discussed by us with reference to the polymerization reaction are not specific to just polymerization processes but are quite applicable to many chain convarsions that can be described by schemes (1)–(3). In a general form the considerations of serviceability criteria for a particular initiator are evidently applicable to any chain reaction.

CONCLUSIONS

The kinetics of induced polymerization are discussed. A relationship is derived linking of initiation with the maximum polymer yield. The results obtained are applied in analyzing experimental findings on the polymerization of styrene and vinyl chloride in the presence of an initiator-activator system (benzoyl peroxide-dimethyl aniline). Conditions conducive to highly efficient initiation are formulated.

Translated by G. CAMERON

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REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH HEAVY METAL SALTS*—III. REACTIONS OF ORGANO-ALUMINIUM COMPOUNDS WITH TITANIUM HALIDES

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(*Received* 23 *April* 1959)

CATALYTIC polymerization has grown considerably in recent years on the basis of catalysts formed by the interaction of a number of organometallic compounds with the salts of multiple valence metals, particularly of organo-aluminium compounds and titanium halides. Oxidizing-reducing reactions between these components lead to the formation of insoluble complexes whose nature determines chain structure in the polymerization of unsaturated compounds. In the case of certain α-olefines two crystalline polymers (isotactic and syndiotactic) and an amorphous polymer are possible. With the dienes the possible number of polymer chain structures is further increased by the formation of *cis* or *trans*-configurations and 1, 2 and 3, 4 structural units.

It has recently been demonstrated that a finished, unsaturated polymer chain formed by diene polymerization is liable to undergo considerable changes, particularly *cis-trans*-isomerization of the structural units under the action of the individual catalyst components [1]. This brings out the necessity for a thorough study of the reactions which determine the chemical composition of a catalyst and hence the efficiency of a system in stimulating polymerization and in determining the structure of the polymer chain.

The first report of a reaction between triethyl aluminium and titanium tetrachloride appears in papers by Ziegler [2, 3] where it is observed that the reaction proceeds at room temperature with the liberation of gaseous products and the formation of a precipitate containing hydrocarbon groups, chlorine, aluminium and titanium.

Natta and co-workers [4] studied the elementary composition of the precipitate formed by the interaction of $Al(C_2H_5)_3$ and $TiCl_4$ in a variety of ratios. These authors showed that as the Al/Cl ratio in the parent mixture rises the Cl/Ti ratio in the precipitate falls off sharply whereas the Al/Ti ratio increases, indicative of more thorough reduction of the $TiCl_4$ by the excess triethyl aluminium. They also established that the composition of the precipitate alters as a function of time.

* Vysokomol. soedin. 1: No. 6, 900–906, 1959.

The authors thus concluded that the elementary composition of the precipitate and consequently its catalytic activity in the polymerization process, are related to the conditions under which the catalyst is prepared. However they failed to study this relationship in greater detail and to ascertain the chemical composition of the precipitate.

The oxidizing-reducing reaction between the catalyst components can result in the formation of a complex mixture of products, particularly $(C_2H_5)_2AlCl$, $(C_2H_5)AlCl_2$, $AlCl_3$, $TiCl_3$, $TiCl_2$ and metallic titanium. In an excess of triethyl aluminium a preferential formation of low valence titanium salts is likely and, in an excess of $TiCl_4$, a preferential formation of aluminium ethyl chloride and aluminium chloride.

Natta holds [4, 5] that the polymerization of olefines under the influence of catalyst complex formation proceeds by an anionic mechanism. At the same time aluminium chloride, which may be present in the catalyst complex, is a typical cationic catalyst. In our laboratory Babitski and Bresler recently found ethyl aluminium dichloride to be a similar catalyst. Thus the reaction between the starting components $Al(C_2H_5)_3$ and $TiCl_4$ of the catalyst may cause the formation of compounds that catalyze the polymerization processes (and secondary reactions in the polymers) by various mechanisms.

The composition of precipitates formed by the interaction of a series of organo-aluminium compounds (mainly ones containing chlorine) with titanium halides has been studied in the present paper.

The experiments were conducted in *iso*-octane at 2–4 per cent concentrations of the starting substances and a temperature of from 20–100°C under argon. On completion of the reaction the precipitate was filtered off, thoroughly washed with solvent and dried to constant weight *in vacuo* at room temperature. The precipitate and the filtrate were then analyzed by the standard methods outlined in the experimental section.

EXPERIMENTAL RESULTS AND DISCUSSION

The interaction of aluminium chloroalkyls with titanium tetrachloride

(a) $Al(C_2H_5)_2Cl + TiCl_4$

The reaction between these components proceeds very slowly. At 20°C the precipitate appears only after 40–50 min. At 80°C the reaction is complete after 3–4 hr. In Table 1 are listed the results pertaining to the composition of the precipitate and the filtrate at $Al(C_2H_5)_2Cl/TiCl_4$ ratios from 0·5 to 2·0. These results show that at all the studied ratios the $TiCl_4$ is reduced no further than $TiCl_3$; $TiCl_2$ does not occur in the precipiate even with a substantial excess of $Al(C_2H_5)_2Cl$. This is borne out by the Cl/Ti ratio in the precipitate: in all experiments it is close to three.

With an excess of $TiCl_4$ (Exp. 5 and 6) it is reduced to Ti^{+3} both by $Al(C_2H_5)_2Cl$ and also by $Al(C_2H_5)Cl_2$ formed in the initial reduction stage. Here

the final reaction product is $AlCl_3$ which is also present in the precipitate. In the remaining experiments, however, the precipitate contains no aluminium. This indicates that the reduction of $TiCl_4$ is, in the first place, caused by the diethyl aluminium chloride and the $Al(C_2H_5)Cl_2$ thus formed reacts with the $TiCl_4$ at a far slower rate. The composition of the products is independent of the reaction temperature over the range 20–80°C.

(b) $Al(C_2H_5)Cl_2 + TiCl_4$

Here the reaction proceeds even more slowly: after 5 hr at 20°C the yield of the interaction products amounts to about 20 per cent. Table 2 gives the results of the experiments which were carried out at different temperatures. These testify that the formation of $TiCl_3$ ($TiCl_2$ is not present in the precipitate) is attended by the appearance in the precipitate of an approximately equivalent amount of aluminium chloride. The presence of the latter is confirmed by the Al : Ti : Cl ratio in the precipitate corresponding to the composition:

$$TiCl_3 + AlCl_3$$

The slight deficiency of aluminium chloride in the precipitate may be explained by its sublimation on drying and also by incomplete precipitation from the filtrate. It is worth noting that in all the experiments a satisfactory balance of products was obtained both with $Al(C_2H_5)Cl_2$ and $Al(C_2H_5)_2Cl$.

The interaction of organo-aluminium compounds with titanium trichloride

The interaction of triethyl aluminium and diethyl aluminium chloride with the violet form of crystalline titanium trichloride was examined. The titanium compound was prepared by the reduction of $TiCl_4$ with hydrogen at 800–850°C followed by washing out and drying *in vacuo*. The character of the interaction was ascertained from the quantity of hydrogen generated on decomposition of the reaction products with dilute HCl in accordance with the scheme:

$$TiCl_3 + HCL \longrightarrow TiCl_3 + {}^1/_2H_2$$

The findings that emerged from this series of experiments are contained in Table 3.

As follows from the Table the activity of the crystalline $TiCl_3$ is very weak in comparison with that of the organo-aluminium compounds. With diethyl aluminium chloride no reaction takes place even with sustained heating whereas triethyl aluminium reduces titanium trichloride to a slight extent only at 100°C.

From the results found in the present paper it can be concluded that the alkyl aluminium halides ($Al(C_2H_5)_2Cl$ and $Al(C_2H_5)Cl_2$) reduce titanium tetrachloride only as far as the trichloride, irrespective of the Al/Ti ratio. At the same time, as demonstrated by Natta [4] and the experiments carried out by us in the laboratory, room temperature is sufficient for triethyl aluminium, in excess, to reduce titanium tetrachloride to the dichloride. A similar reaction

TABLE 1. INTERACTION OF $Al(C_2H_5)_2Cl + TiCl_4$

Expt. No.	Temp. (°C)	Time (hr)	Starting ratio Ti/Al	Starting quantity (mmol)		Comp. of precipitate (mmol)				Comp. of filtrate (mmol)			% of starting elements found		
				$TiCl_4$	$Al(C_2H_5)_2Cl$	Ti^{+3}	Ti^{+2}	Cl′	Al	Ti^{+4}	Cl′	Al′	Ti	Cl	Al
1	20	5	0·6	17·6	29·2	12·1	0	39·6		5	61·0	29·6	97·5	100·7	104·2
2	80	4	0·5	16·0	32·0	16·4	0	50·0	0	0	45·3	31·3	102·0	99·2	98·0
3	80	4	0·9	18·3	20·4	18·6	0	52·6	0	0	39·2	18·9	101·5	98·0	103·0
4	80	7	1·0	20·5	20·5	19·9	0	63·0	0	0	34·7	18·0	97·0	95·5	88·0
5	80	4	2·0	43·0	21·5	42·3	0	183·5	19·0	0	7·8	3·0	98·6	99·0	102·3
6	80	4	2·0	42·0	21·0	42·0	0	173·0	17·0	0	19·8	4·5	100·0	102·0	102·0

TABLE 2. INTERACTION OF $Al(C_2H_5)Cl_2 + TiCl_4$

Expt. No.	Temp. (°C)	Time (hr)	Starting quantity (mmol)		Comp. of precipitate, (mmol)				Comp. of filtrate (mmol)			% of starting elements found		
			$TiCl_4$	$Al(C_2H_5)Cl_2$	Ti^{+3}	Ti^{+2}	Cl′	Al′	Ti^{+4}	Cl′	Al′	Ti	Cl	Al
66	20	5	19·9	19·9	4·6	0	20·6	2·4	15·0	97·8	16·9	98·6	99·3	97·0
65	80	4	23·3	18·9	20·0	0	112·8	16·5	4·0	17·5	1·5	103·0	99·5	95·5

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when the violet form of titanium trichloride is used proceeds at a very slow rate only at 100°C. This leads to the conclusion that the brown form of titanium trichloride formed by the interaction between titanium tetrachloride and or-

TABLE 3. INTERACTION OF $TiCl_3$ WITH ORGANO-ALUMINIUM COMPOUNDS

Organo-aluminium compounds	Temp (°C)	Time (hr)	Starting Al/Ti molar ratio	Amount of $TiCl_3$ % of theoretical
$Al(C_2H_5)_3$	50	2	1 : 1	0
	50	2	1 : 1	0
	90	1	1 : 1	0
	90	5	1 : 1	0
	100	6·5	1 : 1	17
	100	6·5	1 : 1	22
	100	8	1 : 1	18
$Al(C_2H_5)_2Cl$	50	5	1·2 : 1	0
	100	1	1·2 : 1	0
	100	5	1 : 1	0

gano-aluminium compounds is obviously far more reactive with respect to triethyl aluminium than the violet form owing, most likely, to the differences in crystalline structure between the two forms. Actually, as has lately been demonstrated, the violet form of titanium trichloride has a lamellar structure, and the brown form, a fibrous structure [6].

The results of the present work lead to the conclusion that with an excess of titanium tetrachloride in the case of triethyl aluminium, and also with equimolar ratios in the case of alkyl aluminium halides there inevitably occurs the formation of $Al(C_2H_5)Cl_2$ and even of $AlCl_3$ which, as pointed out earlier, are typical cationic catalysts. The presence of these substances can appreciably modify the structure of the polymer.

This postulate is borne out by experiments on the polymerization of butadiene in the presence of $Al(C_2H_5)_2Cl$ and $TiCl_4$. Here, with a molar ratio of Al/Ti less than 1·5 a substantial portion of the aluminium will be in the form $Al(C_2H_5)Cl_2$ and cationic polymerization must then predominate. As the Al/Ti ratio increases the relative portion of $Al(C_2H_5)Cl_2$ will sharply decline and the composition of the catalyst will be practically constant. As shown in our laboratory by Babitski and Bresler the structure of the polybutadiene prepared using the present catalyst system with a slight excess of $Al(C_2H_5)Cl_2$ is independent of the Al/Ti ratio within the range from 3 to 20. Nevertheless at ratios less than unity the polymer differs profoundly from that otherwise obtained in that it is an insoluble, high-melting powder. It is formed when butadiene is polymerized under the influence of ethyl aluminium chloride in the presence of titanium chloride.

EXPERIMENTAL

Starting substances. Solvent—*iso*-octane, "standard" type, b. p. 94·1–94·5°C, n^{20} 1·3914–20, distilled in the presence of metallic sodium and stored over sodium wire under argon.

Triethyl aluminium was separated in the pure form by fractional distillation *in vacuo* of the commercial product. The fraction was removed at 82–83°C/6 mm. For the experiments a 0·1 g/ml solution in *iso*-octane was used and its content of active aluminium [7] and of ethyl groups determined by decomposition with a 5% H_2SO_4 solution.

Analysis results: 80% $Al(C_2H_5)_3 + Al(C_2H_5)_2H$
15–20% $Al(C_2H_5)_2(OC_2H_5)$

Diethyl aluminium chloride was prepared from aluminium *sesqui*chloride [8]. The product was distilled *in vacuo* and the fraction removed at 71–75°C/4 mm. The test solution in *iso*-octane (0·1 g/ml) was analyzed for the chlorine content by Volhard's method.

Dichloroethyl aluminium was synthesized from aluminium *sesqui*chloride and chloride [9]. The product was distilled *in vacuo*, the fraction removed at 76–77°C/8 mm and its chlorine content determined.

%Cl found: 56·5
Calculated for $Al(C_2H_5)Cl_2$ %55·8

Titanium tetrachloride commercial product, "pure", test solution in *iso*-octane, concentration 0·1 g/ml. All solutions were prepared and stored in Shlenk vessels.

Titanium trichloride was obtained by the reduction of $TiCl_4$ with hydrogen at 750–800°C. The product was dried for 15 hr *in vacuo* at 3–4 mm and 150–180°C [10]. On analysis by the permanganate method [11] it proved to contain 98 per cent $TiCl_3$. The product was stored in vials under argon.

Titanium dichloride was prepared by the disproportionation of $TiCl_3$

$$2TiCl_3 \longrightarrow TiCl_4 + TiCl_2$$

at 3–4 mm and 350–450°C.

Argon was rated as containing not more than 0·02 per cent O_2. It was dried with conc. H_2SO_4, phosphorus pentoxide and sodium wire.

TEST PROCEDURE

The experiments to study the interaction of titanium trichloride with organic aluminium compounds were conducted in a flask of 75–100 ml capacity connected to a gas burette. The starting components were added together with the solvent and left to stand at constant temperature for a given length of time, after which the mixture was decomposed by boiling with 0·2N HCL containing $(NH_4)_2SO_4$ to stabilize the $TiCl_3$ against oxidation [11]. The liberated

gas was analyzed for its hydrogen content, a quantity of which likewise formed in the course of the reaction with $TiCl_2$.

The experiments to study the interaction of titanium tetrachloride with organic aluminium compounds were carried out in an apparatus fitted with a stirrer, a "manifold" for adding the starting substances and a siphon connected to an arrangement designed to remove the precipitate and the filtrate: they supplied the total balance of all the elements participating in the reaction.

Analysis of the precipitate. The Ti^{+3} and Ti^{+2} contents were determined from two weighed samples by the permanganate method [11]. From a separate weighed sample dissolved in 5% H_2SO_4 the total titanium content was determined. For this purpose lower forms of titanium were oxidized with hydrogen peroxide to the tetravalent form which was then precipitated with cupferron [12]. The tetravalent titanium was determined from the difference between the total titanium and the sum of the di- and trivalent forms.

The chlorine in the precipitate was determined by Volhard's volumetric method. Ammonium iron alum was added, followed by silver nitrate, in order to oxidize the trivalent titanium to the tetravalent form.

Determination of the aluminium. A weighed portion of the precipitate was dissolved in 5% H_2SO_4 and treated with cupferron. Titanium cupferronate was separated from the solution (containing aluminium) by extraction with chloroform. The solution was neutralized with dry sodium acetate. The aluminium was precipitated out of the neutralized solution with *o*-oxyquinoline. The aluminium *o*-oxyquinolinate was heated in a crucible at 1000–1100°C and converted to Al_2O_3.

The gas liberated on decomposition of the precipitate with 5% H_2SO_4 was analyzed to determine the associated organic radicals in the precipitate.

Analysis of the filtrate. The filtrate was treated with 5% H_2SO_4 and heated to boiling. The gas liberated was measured and in a number of cases analyzed. The hydrocarbon phase was removed and repeatedly treated with 5% H_2SO_4 in a separating funnel until complete absence of chlorine in the washing liquor. The sulphuric acid extracts were reduced a given volume and analyzed for their chlorine, titanium and aluminium contents.

CONCLUSIONS

(1) The products formed by the interaction of the components that go to make up the catalysts used to prepare stereospecific polymers (titanium halides and organo-aluminium compounds) are studied.

(2) On interacting with alkyl aluminium halides, titanium tetrachloride is reduced only to the trivalent state. With ethyl aluminium chloride, moreover, an equivalent quantity of aluminium chloride is formed.

(3) The violet form of $TiCl_3$ fails to react with alkyl aluminium halides, even at 100°C. Under these conditions triethyl aluminium partially reduces $TiCl_3$ to $TiCl_2$.

(4) From a comparison of the findings on the rate of the interaction between titanium tetrachloride and the various organo-aluminium compounds it can be concluded that in decreasing order the reactivity of these latter compounds is as follows:

$$Al(C_2H_5)_3 > Al(C_2H_5)_2Cl > Al(C_2H_5)Cl_2$$

Translated by G. CAMERON

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THE POLYMERIZATION OF UNSATURATED ORGANOSILICON COMPOUNDS *

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(*Received* 9 *May* 1959)

IT is reported in the literature that the vinyl and allyl derivatives of organosilicon compounds do not readily polymerize, irrespective of the position of the double bond relative to the silicon atom and that in the presence of peroxides at a pressure of up to 6000 atm and at about 130°C low molecular weight polymers are formed as viscous oils [1]. It has been demonstrated by ourselves and by other authors too that organosilicon compounds containing a methacryl group are appreciably more reactive and polymerize in the presence of peroxide initiators to yield solid, vitreous polymers [2–5]. The present paper relates to a study of the polymerization of organosilicon compounds containing a methacryl or a carboxyallyl group, and compounds containing the two groups simultaneously. The influence of the distance between the methacryl groups on polymerizability was examined on samples of methacryl derivatives of organosilicon compounds. The compounds selected for polymerization were: 1,2-di-(carboxyallyl methyl)-tetramethyl disiloxane $[CH_2=CH'CH_2OCOOCH_2Si(CH_3)_2]_2O$, 1-methacrylate methyl-2-carboxyallylate methyl tetramethyl disiloxane $CH_2=C(CH_3)COOCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCOOCH_2CH=CH_2$, methacrylate methyl pentamethyl disiloxane $CH_2=C(CH_3)COOCH_2Si(CH_3)_2OSi(CH_3)_3$, 2-methacrylate methyl heptamethyl trisiloxane $(CH_3)_3SiOSi(CH_3)(CH_2OCOC(CH_3)=CH_2)OSi(CH_3)_3$, and dimethacryl derivatives of di-, tri-, tetra- and pentasiloxanes of the general formula $CH_2=C(CH_3)COOCH_2Si(CH_3)_2[O-Si(CH_3)_2]nCH_2OCOC(CH_3)=CH_2$ where $n=1, 2, 3, 4$.

The synthesis of these compounds has been reported earlier [1, 6].

Polymerization was accomplished in dilatometers of about 5 ml capacity at 64·5°C in the presence of benzoyl peroxide. The rate of polymerization was determined from the decrease in volume as a function of the time to attainment of the gelling point.

It follows from our experimental findings that 1,2-di-(carboxyallylate methyl)-tetramethyl disiloxane readily polymerizes (Fig. 1) but its rate is less than

* Vysokomol. soedin. 1: No. 6, 930–933, 1959.

that of 1,2-di-(methacrylate methyl)-tetramethyl disiloxane (Fig. 4, curve 1). A compound containing simultaneously a methacryl and a carboxyallyl group also polymerizes easily with 1-methacrylate methyl -2-carboxyallylate methyl

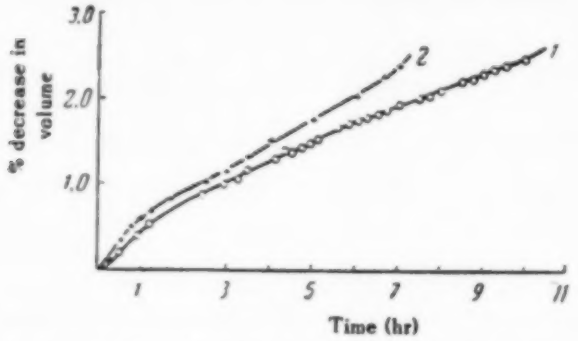

FIG. 1. Polymerization of carboxyallyl esters (3% benzoyl peroxide): (1) 1, 2-di-(carboxyallylate methyl)-tetramethyl disiloxane (2) dicarboxyallyl ester of diethylene glycol.

tetramethyl disiloxane (Fig. 2, curve 1) have a faster rate than 1,2-di-(carboxyallylate methyl)-tetramethyl disiloxane and 1,2-di-(methacrylate methyl)-tetramethyl disiloxane. This phenomenon is obviously attributable to the occur-

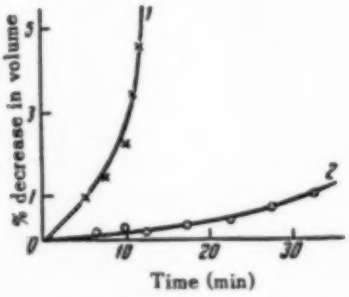

FIG. 2. Polymerization of compounds containing both a carboxyallyl and a methacryl group (0·01% benzoyl peroxide): (1) 1-methacrylate methyl-2-carboxyallylate methyl tetramethyl disiloxane. (2) methacryl carboxyallyl ester of diethylene glycol.

rence of oriented polarization in the vicinity of the disposed polar groups. Comparison of the unsaturated organosilicon compounds, e.g. 1,2-di-(carboxyallylate methyl)-tetramethyl disiloxane ($CH_2=CHCH_2OCOOCH_2Si(CH_3)_2)_2O$, 1-carboxyallylate methyl-2-methacrylate methyl tetramethyl disiloxane and 1,2-di-

(methacrylate methyl)-tetramethyl disiloxane with the corresponding organic compounds of diethylene glycol, viz. dicarboxyallyl ester ($CH_2=CHCH_2OCOOCH_2CH_2)_2O$ methacryl carboxyallyl ester $CH_2=CHCH_2OCOOCH_2CH_2OCH_2CH_2OCOC(CH_3)=CH_2$, and dimethacrylic ester $(CH_2=C(CH_3)COOCH_2CH_2)_2O$, disclosed that $-Si(CH_3)_2-$ is located on the carbon atom combined with the methacryl or carboxyallyl group in place of the $-CH_2-$ group. By comparing the curves for the polymerization processes of the above-mentioned organic and organosilicon compounds (Fig. 1, 2 and 3) the influence of the dimethylsilyl group on the behaviour of the polymerization process can be accounted for. Furthermore the comparison shows that the methacryl organosilicon compounds polymerize far more slowly than their organic analogues (Fig. 4, curves 1 and 6, 2 and 5). Although the polymerization rate of 1,2-di-(carboxyallylate methyl)-tetramethyl disiloxane is less than that of the *bis*-carboxyallyl ester of diethylene glycol (Fig. 1, curve 2) it is still close to the polymerization rate of its organic analogue. It is apparent from the experimental findings on the polymerization of compounds containing a methacryl and a carboxyl group simultaneously that 1-methacrylate methyl-2-carboxyallyl methyl disiloxane polymerizes more readily than the methacryl carboxyallyl ester of diethylene glycol. Thus in the polymerization of dimethacryl derivatives

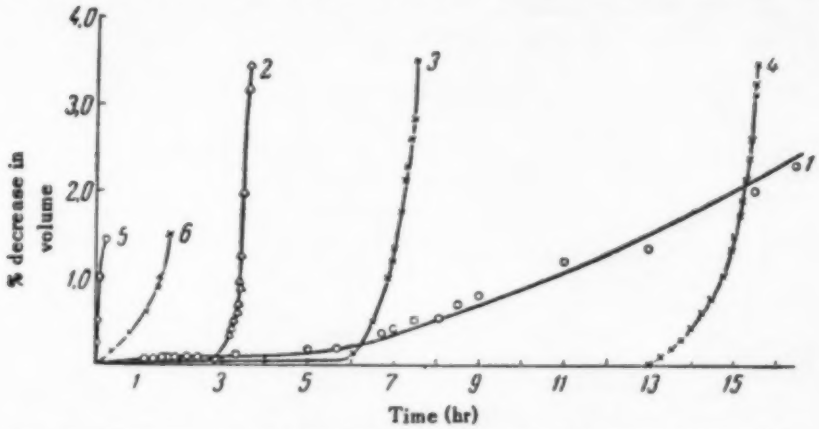

FIG. 3. Polymerization of methacryl derivatives of the siloxane series (0·1% benzoyl peroxide): (1) 1,2-di-(methacrylate methyl)-tetramethyl disiloxane; (2) 1,3-di-(methacrylate methyl)-hexamethyl trisiloxane; (3) 1,4-di-(methacrylate methyl)-octamethyl tetrasiloxane; (4) 1,5-di-(methacrylate methyl)-decamethyl pentasiloxane; (5) dimethacryl ester of triethylene glycol; (6) dimethyacryl ester of diethylene glycol.

of the siloxanes the silicon atom exerts a noticeable inhibiting effect that is substantially weaker in the polymerization of a dicarboxyallyl ester of disiloxane and which totally disappears in the polymerization of 1-methacrylate methyl -2-carboxyallylate methyltetramethyl disiloxane.

The results found from the polymerization of methacryl derivatives of siloxanes with varying distances between the methacryl groups (Fig. 3 curves 1, 2, 3, 4) reveal great differences in the polymerization rates: 1,2-di-(methacrylate methyl)-tetramethyl disiloxane (curve 1) polymerizes more slowly than the 1,3-, 1,4-, and 1,5-dimethacryl derivatives of the tri-, tetra-, and pentasiloxanes. The polymerization rate of 1,3-, 1,4-, and 1,5-dimethacrylate methyl tri-, tetra- and pentasiloxanes decreases inversely with the distance between the methacryl groups, simultaneously accompanied by an increase in the induction period (curves 2, 3 and 4). This appears to stem from the mechanism that is operative for the organic analogues [7, 8] and which is governed by a steric factor.

It follows from the experimental results (Fig. 4) that the monomethacryl derivatives of the siloxane series also polymerize readily and here the rate for

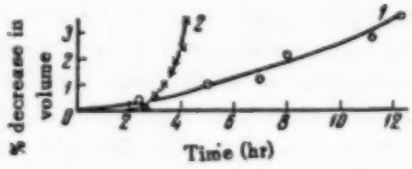

FIG. 4. Polymerization of monomethacryl derivatives of di- and trisiloxanes (0·1% benzoyl peroxide). (1) methacrylate methyl pentamethyl disiloxane; (2) 2-methacrylate methyl heptamethyl trisiloxane.

TABLE 1. THE COMPOSITION OF THE PRODUCTS OF POLYMERIZATION

Original monomer	Content of monomer (%)	Content of polymer (%)	
		soluble	non-soluble
1,2-di-(methacrylmethyl)-tetramethyl-disiloxane	4·8	0·00	95·1
1,3-di-(methacrylmethyl)-hexamethyl trisiloxane	6·60	0·08	94·32
1,4-di-(methacrylmethyl)-octamethyl tetrasiloxane	5·90	0·35	93·76
1,5-di-(methacrylmethyl)-decamethyl pentasiloxane	5·47	0·16	94·36
1,2-di-(carboxiallilate-methyl) tetramethyl-disiloxane	36·70	0·08	63·29
1-methacrylmethyl-2-carboxiallilatemethyl-tetramethyl-disiloxane	23·20	0·03	76·77

2-methacrylate methyl heptamethyl trisiloxane (curve 2) is faster than the rate for methacrylate methyl pentamethyl disiloxane (curve 1). All the polymers were solid, vitreous products. The polymers prepared from the tetrafunctional organosilicon compounds were studied for the content of insoluble and

soluble high molecular compounds. For this purpose weighed samples (1–1·5 g) of the polymers, heated at reaction temperature for 50 hr, were first treated with sulphuric ether in a Scxhlet apparatus to extract the monomer, and then with acetone to remove the soluble polymer.

Our experimental findings (listed in the Table) show that the conversion for the dimethacryl derivatives of the siloxane series is 95–94 per cent; for the compounds containing a carboxyallyl group, 63–77 per cent: for the insoluble polymers in the case of the carboxyallyl derivatives it is governed by the incompleteness of polymerization under the given reaction conditions.

CONCLUSIONS

(1) The polymerization of unsaturated organosilicon compounds is studied. Compounds which contain methacryl groups, carboxyallyl groups and also carboxyallyl and methacryl groups simultaneously in the hydrocarbon radical located on the silicon atom readily polymerize in the presence of peroxide initiators.

(2) Of the compounds studied the dimethylsilyl group has an extremely pronounced inhibiting influence on the polymerization of the dimethacryl derivatives of di- and trisiloxane.

(3) The polymerization rate of the dimethacryl derivatives of the siloxane series diminishes from 1,3-di-(methacrylate methyl)-hexamethyl trisiloxane to 1,5-di-(methacrylate methyl)-decamethyl pentasiloxane and 1,2-di-(methacrylate methyl)-tetramethyl disiloxane polymerizes less readily than its homologues.

Translated by G. CAMERON

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 1, No. 4, 1959*

ON HETEROCHAIN POLYAMIDES—XVI. POLYAMIDES CONTAINING THE SILOXANE GROUP IN THE PRINCIPAL CHAIN

T. M. Frunze, V. V. Korshak, D. N. Andreev, E. V. Kukharskaia, Vysokomol. soedin. 1: No. 4, 489–494, 1959.

A NUMBER of homogeneous and mixed polyamides containing siloxane groups in the principal chain have been prepared. Incorporation of the siloxane group causes a sharp fall in the flow temperature.

Polyamides containing aliphatic units only are transparent and are distinguished by a high elasticity. In the course of time crystallization gradually sets in, accompanied by growing turbidity and decreasing elasticity of the specimens. This is due both to the high flexibility of the siloxane chains, as well as to the presence of side chain substitutents at the silicon atom, hindering chain ordering.

ON HETEROCHAIN POLYAMIDES—XVII. POLYAMIDES FROM *p*-XYLYLENEDIAMINE

T. M. Frunze, V. V. Korshak, E. A. Krasnianskaia, Vysokomol. soedin. 1: No. 4, 495–499, 1959.

POLYAMIDES have been synthesized from *p*-xylylenediamine and various aliphatic and aromatic acids. In general the reaction products are opaque substances, often coloured to a certain extent and with quite high melting temperatures. The polyamide prepared from the salt of *iso*phthalic acid is amorphous. With increasing number of methylene groups in the dicarboxylic acid molecule, the flow temperature of the polymers containing acid residues with an even number of methylene groups is always higher than in the case of polymers obtained from acids with an odd number of the groups.

Mixed polyamides obtained from the salts of sebacic acid with *p*-xylylenediamine and hexamethylenediamine exhibit a linear relation between the flow temperature and the composition, being an example of the system of isomorphous polyamides.

ON HETEROCHAIN POLYAMIDES—XVIII. FORMATION OF MIXED POLYAMIDES DURING MELTING OF THE HOMOCHAIN COMPOUNDS

T. M. Frunze, V. V. Korshak, V. A. Makarkin, Vysokomol. soedin. 1: No. 4, 500–505, 1959.

THE interaction between homochain polyamides on their being heated at temperatures above melting has been investigated. Determinations were made of the change in the flow temperature, in the ratio of soluble and insoluble fractions, in the crystallinity and in the solubility of the products with increasing time of heat treatment. In the course of the heating process, block copolymers are evidently formed first, changing on subsequent heating to ordinary mixed copolymers, viz., mixed polyamides. The block copolymers have a short life ~3–5 hr.

* English abstracts reprinted from Vysokomol. soedin. 1: No. 4, 1959.

With increasing heating periods, the flow temperature of the polymers formed diminishes; the solubility and ultimate elongation increase and the strength falls.

THE HYDROGEN BOND AND THE POLYMERIZATION CAPACITY OF *o*-,*m*- AND *p*-SUBSTITUTED N-PHENYLMETHACRYLAMIDES—III

T. A. Sokolova, G. M. Chetyrkina, V. N. Nikitin, Vysokomol. soedin. **1**: No. 4, 505–510, 1959.

THE authors have shown in a previous paper that *m*- and *p*-ethoxy-N-phenylmethacrylamides, of which the molecules possess intermolecular hydrogen bonds, polymerize in bulk much slower than the *o*-isomers, of which the molecules are unassociated.

In the present study the polymerization has been investigated of *o*-, *m*-, and *p*-carbethoxyphenylmethacrylamides (CEPMA) with substituents opposite in character to the alkoxy group.

Examination of the infra-red spectra of these monomers showed that *m*- and *p*-CEPMA have intermolecular hydrogen bonds in the condensed state, partially disrupting on solution. In *o*-CEPMA, intramolecular hydrogen linkage has been revealed, forming a stable 6-membered ring, owing to which the molecules remain isolated.

It has been established dilatometrically that in this case *o*-CEPMA polymerizes faster than its isomers. Thus the effect of the intermolecular hydrogen bond on the polymerization process prevails over the electronic effect of the substituent in the phenyl residue of the monomer.

The predominant influence of the intermolecular hydrogen bond on the polymerization rate has also been confirmed by studies on a number of tolylmethacrylamides (TMA).

It has been found that in this case the molecules of all three isomers are associated; the polymerization rate for all of them being the same.

INVESTIGATION INTO THE PROCESS OF THE HARDENING OF ORGANOSILICON RESINS—I. HARDENING OF THE RESIN PREPARED BY HYDROLYSIS AND CONDENSATION OF TETRAETHOXYSILANE

A. A. Tager, A.P. Bochkareva, N. M. Dvoretskaia, Vysokomol. soedin. **1**: No. 4, 511–517, 1959.

THE hardening of organosilicon resins was studied by means of thermomechanical curves obtained with the aid of the dynamometric Kargin balance. It has been shown that similarly to resol, low molecular linear condensation products may exist in three physical states: vitreous, high elastic and viscoplastic. The sequence of the states as a function of the temperature is: vitreous, viscoplastic, high elastic (due to formation of cross linkages) and vitreous (hardening). Gelatinized condensation products, like resitol, may exist only in two physical states, namely, vitreous and high elastic. Sequence: vitreous, high elastic and vitreous (hardening). With increase in the degree of condensation the vitrification temperature rises from −140 to −60°C the hardening temperature falls from 200 to 100°C and the high elasticity modulus increases.

ON HETEROCHAIN POLYAMIDES—XIX. POLYAMIDES FROM THE *cis*-AND *trans*-ISOMERS OF 1,3-DIAMINOCYCLOHEXANE AND ALIPHATIC DICARBOXYLIC ACIDS

T. M. Frunze, V. V. Korshak. Z. V. Romanova, Vysokomol. soedin. **1**: No. 4, 518–525, 1959.

POLYAMIDES have been prepared from the salts of the *cis*- and *trans*-isomers of 1,3 diamino-

cyclohexane and adipic, azaelic and sebacic acids. All polyamides obtained from the *trans*-isomers had higher melting temperatures and were more crystalline and less soluble than the polyamides from the *cis*-isomers.

A study of the properties of mixed polyamides produced from *cis*-and *trans*-isomers in different ratios showed that the compounds containing the *trans*-isomer up to 40 per cent are transparent, soluble products further increase in the *trans*-isomer content of the polyamide leading to loss of solubility and increase in crystallinity.

Mixed polyamides have also been obtained, containing hexamethylenediamine in addition to the *cis*- or *trans*-1,3-diaminocyclohexane.

THE EFFECT OF THE COMPOSITION OF MIXED POLYAMIDES ON THEIR PHASE STATE

G. L. Slonimskii, T. M. Frunze, V. V. Korshak, L. Z. Rogovina, Vysokomol. soedin. **1**: No. 4, 526–529, 1959.

A STUDY has been made of the change in phase of mixed polyamides obtained by the copolycondensation of diammonium hexamethyleneadipinate and diammonium hexamethylene*iso*phthalate (HPh) in relation to the composition of the system. With change in the mixed polyamide composition a transition has been shown to take place from the crystalline polyhexamethyleneadipinamide to the amorphous polyhexamethylene*iso*phthalamide. The melting temperature falls, the vitrification temperature passes through a minimum and the crystallinity gradually decreases, vanishing completely at an HPh content equal to 50 mole %. In the process of transition from the crystalline to the amorphous polymers, the existence of an elastic state in a certain region of the crystalline state is observed.

The necessity has been stressed of theoretical and experimental study of the mechanism of transition from one phase state to another with change in composition of mixed polyamides.

THERMOMECHANICAL STUDY OF POLYAMIDES FROM *cis*- AND *trans*-ISOMERS OF DIAMINOCYCLOHEXANE AND ALIPHATIC DICARBOXYLIC ACIDS

G. L. Slonimskii, T. M. Frunze, V. V. Korshak, Z. V. Romanova, L. Z. Rogovina, Vysokomol. soedin. **1**: No. 4, 530–533, 1959.

PHASE transitions in the system of mixed polyamides obtained from dicarboxylic acids and *cis*-and *trans*-isomers of 1,3-diaminocyclohexane have been studied with the aid of the thermomechanical and X-ray analysis methods.

In all cases investigated, of the two extreme polymers with respect to composition, one is crystalline and the other amorphous.

With change in the quantitative composition of the polymers, sharply defined transition takes place from the group of crystalline polyamides to that in the amorphous state. Owing to the complex structure of the polymer and the intertwining in it of crystalline and amorphous regions over a certain range of composition, superposition of the crystalline on the amorphous states takes place, which is manifested in the existence of a well expressed vitrification temperature alongside a melting temperature and also in the origin and development of an elastic state within the limits of the crystalline state.

MUTUAL SOLUBILITY OF POLYMERS—V. MECHANO-CHEMICAL COMPATIBILITY

G. L. Slonimskii, E. V. Reztsova, Vysokomol. soedin. **1**: No. 4, 535–538, 1959.

A STUDY has been made of the properties of rubbers obtained on the basis of combinations of SKS-30A and SKB elastomers under various conditions of severe mechanical treatment in the presence and in the absence of oxygen.

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It has been shown that alongside the mixing of the two polymers mechano-chemical blending takes place, analogous to the mechano-chemical process of preparing graft and block polymers. It has been shown that in the case of mutually insoluble polymers, depending upon the relation between these two mechanisms for the mixing of polymer chain molecules, one may obtain both the earlier investigated microheterogeneous mixtures possessing characteristic anomalous properties, as well as mixtures in which the anomalies are absent.

THE EFFECT STRUCTURATION ON THE CRYSTALLINE STATE OF GUTTA-PERCHA

B. A. Kargin, Z. I. Sogolova, B. I. Aikhodzhaev, Vysokomol. soedin. **1**: No. 4. 539–541, 1959.

THE change in the melting temperature, temperature of disorientation and the mechanical properties of gutta-percha have been studied with respect to the bound sulphur content.

Increase in bound sulphur (up to 3·1 per cent) has been shown to change the melting temperature of the crystals insignificantly, but to have a marked effect on the temperature of disorientation of oriented crystals.

Structuration leading to decrease in the elasticity modulus and the recrystallization stress, is evidently associated with decrease in the degree of crystallization of the gutta-percha.

INVESTIGATION OF THE DIELECTRIC LOSSES IN POLYMETHYLACRYLATE AND IN POLYVINYLACETATE

L. V. Krasner and G. P. Mikhailov, Vysokomol. soedin. **1**: No. 4, 542–548, 1959.

A STUDY has been made of the dielectric losses and the polarization in the vitreous and elastic states of the polymethylacrylate (PMA) and polyvinylacetate (PVA) polymers, differing in the structure of the side chain polar radical. Runs were made over the range of frequencies 20 Hz–100 kHz and of temperatures 120°–180°C.

It has been found that the more flexible side chain radical of PVA facilitates a stronger correlation of the vitreous state, leading to an increase in the duration of relaxation and a decrease in $(\mu\overline{V^2})$ of PVA as compared to the $(\mu\overline{V^2})$ of PMA.

A treatment of the data based on the circular diagram method made it possible to establish the existence of dipole-radical losses superimposing on the dipole-elastic state at temperatures above the vitrification temperature T_g.

THE EFFECT OF MOISTURE ON THE DIPOLE-RADICAL LOSSES IN POLYVINYLACETATE

L. V. Krasner, G. P. Mikhailov, Vysokomol. soedin. **1**: No. 4, 558–562, 1950.

THE effect of the presence of varying amounts of moisture in polyvinylacetate (PVA) on the dipole-radical losses has been investigated. It has been established that in dry PVA the region of maximum dipole-radical losses appears only in the case of low frequencies, of the order of 20-25 Hz and may be associated with the motion of polar side chains.

The effect of moisture on the dipole-radical losses consists in the appearance of two relaxation processes in the polymer-water system, of which one is due to the motion of the acetate side chains, as in the dry polymer, and the other to the molecular relaxation of the water bound to the PVA macromolecules.

Investigation of the dipole-elastic losses of moist PVA showed that in this case there is only a single relaxation process, associated with the motion of the polymer molecules, the water exerting a plasticizing effect on the polymer.

INVESTIGATION OF THE DIELECTRIC RELAXATION IN METHACRYLATE-STYRENE COPOLYMERS

T. I. Borisova, G. P. Mikhailov, Vysokomol. soedin. **1**: No. 4, 563–573, 1959.

THE temperature-frequency correlations of the generalized dielectric constant of methylmethacrylate-styrene copolymers with the content of the polar component varying from 18 to 99·2 per cent (by weight) have been presented.

It has been shown that the relaxation times of the dipole-elastic and dipole-radical processes diminish with increasing styrene content. The parameters of the distribution of the relaxation times for both processes have been calculated with the aid of the circular diagrams method and of the Fuoss-Kirkwood theory. The values for the apparent activation energies have been calculated. An explanation of the correlations observed has been advanced.

INVESTIGATION OF THE EFFECTIVE DIPOLE MOMENTS OF METHYLMETHACRYLATE-STYRENE COPOLYMERS

T. I. Borisova, G. P. Mikhailov, Vysokomol. soedin. **1**: No. 4, 574–581, 1959.

WITH the aid of the circular diagram and the Fuoss and Kirkwood methods the effective dipole moments of the methylmethacrylate monomer unit as a function of its concentration in the copolymer with styrene has been calculated on the basis of the temperature frequency correlations of the generalized dielectric constant. With growth in concentration of the methylmethacrylate the values of the effective dipole moments corresponding to the molecular relaxation of the vitreous state of the polymer increase, whereas the analogous quantities for the case of the high state diminish.

No changes in the effective dipole moments with the temperature have been observed in the temperature range investigated.

SYNTHESIS OF SULPHUR COMPOUNDS ON THE BASIS OF VINYL ETHERS AND ACETYLENE—XX. THE INTERACTION OF MERCAPTALS WTH VINYL SULPHIDES AND VINYL ETHERS

M. F. Shostakovskii, E. N. Prilezhaeva, V. M. Karavaeva, Vysokomol. soedin. **1**: No. 4, 590–593, 1959.

POLYALKYLMERCAPTOALKANES are formed in good yields on the interaction of mercaptals with vinylalkylsulfides in the presence of the etherate of boron fluoride. The yield the monoadduct was considerably higher than in the reaction of the oxygen compounds under analogous conditions. This is explained by the fact that sulphurized vinyl compounds possess a reduced capacity for ionic polymerization.

Activation of the double bond of a vinyl ether by the etherate of boron fluoride has been shown to proceed easier than cleavage of a mercaptide ion from a mercaptal molecule, since in a mercaptal medium the vinyl ether yields a low molecular polymer with mercaptal end groups.

SYNTHESIS OF SULPHUR COMPOUNDS ON THE BASIS OF VINYL ETHERS AND ACETYLENE—XXI. COPOLYMERIZATION OF VINYL SULPHIDES WITH STYRENE AND VINYLBUTYL ETHER IN ACCORDANCE WITH THE IONIC MECHANISM

M. F. Shostakovskii, E. N. Prilezhaeva, V. M. Karavaeva, Vysokomol. soedin. **1**: No. 4, 594–596, 1959.

EXPERIMENTS have been made on the ionic copolymerization in bulk of vinylethyl and of vinylphenyl sulphides with vinylbutyl ether and styrene in the presence of ferric chloride.

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It has been shown that vinylethyl sulphide manifests less activity in ionic polymerization than vinylphenyl sulphide and styrene less than vinylbutyl ether.

DIFFUSION, VISCOSITY AND MOLECULAR DIMENSIONS OF POLYDIMETHYLSILOXANE IN SOLUTION

V. N. Tsvetkov, P. K. Chander, Vysokomol. soedin. **1**: No. 4, 607–612, 1959.

In the work the diffusion coefficients D and intrisic viscosities $[\eta]$ of fractions of PDMS in tetrachloromethane have been determined. The molecular weights M_w of the fractions were obtained by the light scattering method and a relationship was found between M, D and $[\eta]$.

With the aid of the relationship the dimensions of the PDMS macromolecules in tetrachloromethane could be calculated, being found less than those of vinyl polymers of the same degree of polymerization.

OSMOMETRIC DETERMINATION OF THE MOLECULAR WEIGHTS OF POLYMERS AT ELEVATED TEMPERATURES

I. S. Gil'man, Z. A. Rogovin, Vysokomol. soedin. **1**: No. 4, 619–622, 1959.

An osmometer is described suitable for the rapid measurement of osmotic pressures in polymer solutions at elevated temperatures by the static method. To judge of the functioning of the osmometer, molecular weight determination of two fractions of polypropylene have been carried out at 115°C.

RELATION BETWEEN THE MOLECULAR WEIGHT OF POLYMERS AND THE VISCOSITY OF THEIR SOLUTIONS

S. A. Pavlova, S. R. Rafikov, Vysokomol. soedin. **1**: No. 4, 623–626, 1959.

It has been shown on polyamides as example that in the generally accepted formula for viscosity $[\eta]=KM^{\alpha}$ the constants K and α are correlated in accordance with the equation $K=1{\cdot}32(2{\cdot}4\times10^{-5})^{\alpha}$. Comparison of the equation with published values for K and α for all synthetic polymers has shown the equation $[\eta]=\frac{21}{m_0}(40\times10^{-5}\frac{M}{m_0})^{\alpha}$, where m_0 is the mean weight of a chain unit, to be valid.

CROSS LINKING OF POLYETHYLENE BY THE ACTION OF ULTRA-VIOLET LIGHT IN THE PRESENCE OF SENSITIZERS

Tsyan' Bao-Gun, Chian Pin-Chen, Khou En-Chien, Vysokomol. soedin. **1**: No. 4, 635–640, 1959.

The melting temperature of polythylene may be raised from 115 to 250° with the aid of cross linkage brought about by sensitized irradiation with ultra-violet light. Benzophenon and diphenylamine were used as sensitizers, the former, yielding free phenyl radicals being the more effective. It is proposed that sensitized cross linking proceeds through an intermediate stage of free radical formation. In such case simultaneous photochemical cross linking and disintergration is not excluded.

The dependence of the degree of sensitized cross linking on the concentration of the sensitizer added is insignificant. The degree of cross linkage depends mainly on the duration of the irradiation. The degree of cross linkage was determined from data on the change in thermomechanical properties and solubility. It has been shown that the mean number of cross linked units and also the coefficient of cross linkage is a logarithmic function of the irradiation time.

CARBOCHAIN POLYMERS AND COPOLYMERS—XV. SYNTHESIS AND POLYMERIZATION OF THE ESTERS OF VINYLPHOSPHINIC ACID

H. S. Kolesnikov, E. F. Rodionova, Vysokomol. soedin. **1**: No. 4, 641–646, 1959.

THE *n*-propyl, *iso*propyl, *iso*amyl, *n*-hextyl and *sec*-octyl esters of vynylphosphinic acid have been synthesized and the polymers of these esters (excepting *sec*-octyl) and of the earlier synthesized methyl, ethyl, *n*-butyl and *iso*butyl esters of this acid, have been obtained by polymerization in the presence of benzoyl peroxide. It has been found that with increasing length of the *n*-alkyl radical of the ester of vinylphosphinic acid, the vitrification temperature of the polymer falls. The rate of polymerization of the esters of vinylphosphinic acid increases with the length of the principal chain of the alkyl group; an exception is the methyl ester.

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ON HETEROCHAIN POLYESTERS – XVIII. POLYESTERS OF *o*-XYLYLENGLYCOL

S. V. Vinogradova, V. V. Korshak, Vysokomol. soedin. **1**: No. 5, 649–655, 1959.

THE synthesis and study have been carried out of polyesters of *o*-xylylenglycol and aliphatic and aromatic acids of various structure. The effect of the reagent structure on the properties of the polyesters has been discussed. Comparison of the polyesters of *o*-xylylenglycol with the corresponding polyesters of tetramethylenglycol and *p*-xylenglycol showed that the former largely possessed lower softening temperatures than the latter, which evidently is connected with diminished packing density of the polymer chains of the *o*-xylylenglycol polyesters, owing to the *ortho*-position of the methylol groups in the glycol. The polyesters of *o*-xylylenglycol and aliphatic dicarboxylic acids are dense, viscous liquids; the polyesters of *o*-xylylenglycol and aromatic dicarboxylic acids amorphous solids.

ON HETEROCHAIN POLYESTERS – XIX. POLYESTERS OF QUINITE

S. V. Vinogradova, V. V. Korshak, Vysokomol. soedin. **1**: No. 5, 656–661, 1959.

THE synthesis and study have been carried out of polyesters of quinite and aliphatic and aromatic dicarboxylic acids of various structure. The effect of the reagent structure on the polyester properties has been discussed. Polyesters of *trans*-quinite are solids with higher softening temperatures than those of the corresponding polyesters of tertamethylenglycol. The polyesters of *cis*-quinite are characterized by lower softening temperatures than the corresponding polyesters of *trans*-quinite. The properties of the quinite polyesters have been shown to be intimitely connected with the structure of the dicarboxylic acid used in their synthesis.

INTERACTION OF CELLULOSE WITH LIQUIDS

K. P. Mischenko, S. L. Talmud, V. I. Iakimova, Vysokomol. soedin. **1**: No. 5, 662–669, 1959.

THE heats of interaction of various kinds of cellulose with different liquids have been measured in an ordinary type of calorimeter. From the heat effects the values for the specific surface area of cellulose have been calculated and the results compared with experimental determinations. It has been pointed out that the specific surface area of cellulose cannot be calculated from the heat effect, since the latter is the sum of a number of effects associated with different processes taking place on contact of the cellulose with liquid. The heat of adsorption has been calculated. On adsorption of water vapor it constitutes ~3 per cent of the over-all heat effect as determined calorimetrically.

* English abstracts reprinted from Vysokomol. soedin. **1**: No.5, 1959.

ORGANOPHOSPHOROUS POLYMERS—VI. POLYAMIDES OF SOME PHOSPHORUS-CONTAINING DICARBOXYLIC ACIDS

T. M. Frunze, V. V. Korshak, V. V. Kurashev, Vysokomol. soedin. **1**: No. 5, 670–676, 1959.

POLYAMIDES have been obtained from phosphorus-containing dicarboxylic acids of the type $RP(O)(C_6H_4COOH)_2$, R being C_6H_5 or CH_3, and a number of aliphatic and aromatic diamines. It was found that substitution of the methylene by the P(O)R group in the dicarboxylic acid considerably raises the melting temperature of the polyamides.

Polyamides from diacids with *p*-position of the functional groups possess higher melting temperatures and poorer solubilities than polyamides of acids with *m*- and *o*-positions. Substitution of the CH_2 at the phosphorus atom of the acid is accompanied by a rise in the melting temperature of the polyamides.

Pulyamides obtained from aromatic diamines have been shown to possess higher melting temperatures than those from the aliphatic compounds. The usual effect on the polyamides of the odd and even number of carbon atoms in the case of the aliphatic diamines as well as of the position of isomerism of the functional groups in the case of the aromatic diamines also hold for this case.

ORGANOPHOSPHORUS POLYMERS—XII. MIXED PHOSPHORUS-CONTAINING POLYAMIDES

T. M. Frunze, V. V. Korshak, I. V. Kozlov, V. V. Kurashev, Vysokomol. soedin. **1**: No.5, 677–681, 1959.

BINARY and ternary systems of phosphorus-containing polyamides have been obtained from salts of *bis*-(*p*-carboxyphenyl) phenylphosphine oxide and of *bis*-(*p*-carboxyphenyl: methylphosphine oxide with hexamethylenediamine and salts of the dicarboxylic acids) adipic, azelaic and sebacic, with the same diamine and also with ε-caprolactam.

Changes in the properties of the mixed phosphorus-containing polyamides obey the rules common to property changes in mixed polyamides. Varying the molar ratio to the reagents changes of solubility and softening and melting temperatures of the mixed phosphorus-containing polyamides. Of the binary system (of mixed phosphorated polyamides) minimum melting temperature is possessed by polymers containing 40 mole % of the residues of the salts of phosphorated dicarboxylic acids and hexamethylenediamine.

With ternary systems of mixed phosphorus-containing polyamides the region of polymers with lower melting temperatures is at about the center of the composition-properties triangle, shifted in the direction representing the system with minimum melting temperature.

INTERACTION OF GELATINE AND FORMALDEHYDE

V. A. Pchelin, M. A. Salimov, Vysokomol. soedin. **1**: No. 5, 682–687, 1959.

THE interaction of gelatine and formaldehyde at pH 11·9 and 4·5 is responsible for a number of changes in the infra-red spectrum of the former. The greatest change is observed at pH 11, resulting in increase of absorption over a wide region of the spectrum; after washing the specimens with water part of the absorption disappears, whereas part remains. The irreversible changes are interpreted as the result of increase in the number of C—C and C—N bonds. Similar change is caused by treatment at pH 9. However the post-washing absorption is weaker than in the case of pH 11. Treatment of the gelatine at pH 4·5 does not bring about irreversible changes in the spectrum.

THE EFFECT OF THE NATURE AND QUANTITY OF EMULSIFIER ON THE RATE OF EMULSION POLYMERIZATION OF STYRENE

Chzhan Zsin-yui, Chen Tse, Sun' Tsya-chzen, Gao Go-tsin, Vysokomol. soedin. 1: No. 5, 698–703, 1959.

A STUDY has been made of the effect of the nature and quantity of emulsifier on the rate of emulsion polymerization. It has been found that the surface of the polymer particles depends upon the nature of the emulsifier, while the surface of the polymer-monomer particles determines the rate of polymerization. The results confirm the assumption as to the polymerization taking place in the adsorption layer of the polymer-monomer particles.

CONDENSATION OF ORGANOSILICON DICARBOXYLIC KETO ACIDS WITH GLYCOL

K. A. Andrianov, A. A. Zhdanov, V. A. Odinets, Vysokomol. soedin. 1: No. 5, 704–710, 1959.

A METHOD has been described for the synthesis of diketodicarboxylic acids with varying content of dimethylsiloxane units and the polycondensation of *bis* (*o*-carboxyphenylketobenzyl) dodecamethylhexasiloxane with glycol and maleic anhydride has been investigated.

It has been established that on prolonged polycondensation of glycol with the dicarboxylic acids containing more than two dimethylsiloxane units, a rearrangement occurs with the formation of polydimethylsiloxanes and polyesters with disiloxane units.

GEL FORMATION IN METHANOL SOLUTIONS OF POLYMETHACRYLIC ACID

Yu. S. Lipatov and P. I. Zubov, Vysokomol. soedin. 1: No. 5, 711–714, 1959.

THE specific viscosity of methanol solutions of polymethacrylic acid at concentrations up to 5% has been investigated at 20 and 55° with respect to the degree of neutralization. It has been found that addition of NaOH to a solution of low concentration leads to decrease in the specific viscosity owing to decrease in solubility in methanol of the partially neutralized polymethacrylic acid and coiling of the polymer chain. At concentrations above 5% and degree of neutralization 10%, gel formation takes place on heating. The heat of aggregation is about 20,000 cal/mole. Gel formation in methanol solutions of polymethacrylic acid is observed to take place at room temperature on adding strontium oxide to 3% solutions in amounts comprising 5% with respect to the carboxyl groups. The conclusion has been drawn that a general condition for gel formation is the change of solubility in the given solvent of constituent groups of the polymer molecule.

A STUDY OF THE PACKING DENSITY OF COTTON CELLULOSE PREPARATIONS

V. S. Sharkov, V. P. Lævanova, Vysokomol. soedin. 1: No. 5, 730–737, 1959.

THE supermolecular structure of natural, mercerized and dry ground cotton cellulose has been investigated by following the changes in density of the residues in the course of passage of the cellulose into solution during alcoholysis and hydrolysis. With the aid of this method the presence has been shown of strained regions in the cellulose preparations, the preparations increasing in density on breakdown of these regions. After ultimate packing has set in the specific weight of the cellulose exhibits no further change up to the end of the alcoholysis or hydrolysis process.

It has been shown that during dry grinding the cellulose preparations have a tendency to form looser structures. The latter becomes denser in the presence of water. Still close packing under the influence of water is hindered by hydrogen bonding between the macromolecules of the loose preparations.

ANALYSIS OF α-METHYLSTYRENE-STYRENE COPOLYMERS BY THE INFRA-RED ABSORPTION SPECTRA IN THE REGION OF 3 μ

E. I. Pokrovskii, Vysokomol. soedin. **1**: No. 5, 738–739, 1959.

A PROCEDURE has been developed for the quantitative determination of the α-methylstyrene and styrene residues in the copolymers from the absorption bands at 2986 and 2850 cm^{-1}. Pure polystyrene and poly-α-methylstyrene were used as reference substances and a number of their mechanical mixtures was employed for checking.

DISINTEGRATION OF FIBRES BY MECHANICAL ACTION

A. V. Orlova, V. A. Berestnev, V. A. Kargin, Vysokomol. soedin. **1**: No. 5, 740–742, 1959.

THE mechanism of disintegration of capron cord fibres by mechanical action has been studied with the aid of a polarization microscope. It has been found that disintegration of the cord differs on single and repeated treatment. It is suggested that twist exerts considerable influence on the appearance of defects in the fibre during fatigue. Disintegration of cord in a tyre has been shown to take place according to the same mechanism as disintegration of fibres on repeated cyclic stretching.

POLYTITANOORGANOSILOXANES

K. A. Andrianov, E. Z. Asnovich, Vysokomol. soedin. **1**: No. 5, 743–747, 1959.

A STUDY has been made of the properties of polyphenylsiloxane polymers containing silicon, oxygen and titanium atoms in the principal chains of the molecules.

It has been shown on determination of the thermomechanical properties that the polymers do not give rise to flow but that they dissolve well in organic solvents.

Polytitanophenylsiloxanes are highly stable towards the action of aqueous solutions of hydrochloric acid.

SOME THERMOMECHANICAL PROPERTIES OF ISOTACTIC POLYPROPYLENE

M. P. Zverev, V. S. Klimenkov, Vysokomol. soedin. **1**: No. 5, 758–760, 1959.

THE region of the high elastic state of the ether-soluble fraction of isotactic polypropylene does not change on adding low molecular substances (plasticizers), which is characteristic of amorphous polymers.

The effect of plasticization of crystalline polypropylene is observed at temperatures close to melting of the crystalline regions of the polymer. The introduction of low molecular compounds leads to a lowering of the melting temperature of the crystalline polymer. The melting temperature of crystalline polypropylene depends upon the ratio of the stereoregular and atactic structures.

TIME DEPENDENCE OF THE STRENGTH OF POLYMETHYLMETHACRYLATE

M. I. Bessonov, M. P. Kuznetsov, Vysokomol. soedin. **1**: No. 5, 761–768, 1959.

DATA are presented on the effect of preliminary orientation on the time dependence of the strength of polymethylmethacrylate (PMMA). The mechanical durability of PMMA greatly increases, and the laws governing the time dependence of the strength of PMMA change as the result of preliminary orientation. This change is associated with the considerable deformation of the oriented PMMA specimens during the tests. The effect of temperature on the

time dependence has been compared for the oriented and isotropic PMMA. Uniaxially oriented PMMA has been shown to possess anisotropy of mechanical durability and to be practically isotropic with respect to the elastic properties. Data have been produced on the time dependence of strength for uniaxial and planar oriented PMMA of the same degree of orientation. The agreement between mechanisms of polymer strengthening through orientation and the experimental data has been discussed.

SOME CORRELATIONS IN THE VITRIFICATION OF RUBBERS

G. M. Bartenev, Yu. A. Gorbatkina, Vysokomol. soedin. **1**: No. 5. 769–775, 1959.

THE inverse temperature of vitrification of rubber ($1/Tg$) depends linearly on the logarithm of the rate of cooling. The activation energy of vitrification of rubbers, as of other amorphous polymers, is proportional to the vitrification temperature.

The coefficients of expansion outside the limits of vitrification and the temperature range of the vitrification region are practically independent of the cooling rate. The change a length of the specimen, however, is the greater, the faster the cooling.

DETERMINATION OF THE CRITICAL COMPOSITION OF THE SYSTEM POLYMETHYLMETHACRYLATE-ACETONE-ETHYL ALCOHOL

O. V. Kallistov, M. G. Okuneva, Vysokomol. soedin. **1**: No. 5, 776–780, 1959.

THE light scattering of the tri-component system polymethylmethacrylate-acetone-ethyl alcohol has been measured. As specimens, fractions of polymethylmethacrylate were employed, obtained by the method of fractional precipitation. The relation obtained between Hc/R''_{90} and the concentration of the binary solvent enabled the calculation to be made of the second virial coefficients A_2 and of the molecular weight $\overline{M}_B$. The volume fraction of the precipitant has been determined $\varepsilon_k = 0{\cdot}5$ corresponding to the critical state of the system, i.e. to the condition $A_2 = 0$ at the temperature 19°C. An estimation of the degree of coilage of the polymethylmethacrylate macromolecules has been made from the ratio of the undisturbed size h_0 to the size corresponding to free rotation h_f. The possibility has been shown of determining the molecular weights of polymethylmethacrylate in the binary solvent (acetone-ethyl alcohol).

DETERMINATION OF THE RELATIVE ACTIVITY COEFFICIENTS IN THE COPOLYMERIZATION OF VINYLETHYLSULPHIDE WITH STYRENE AND METHYLMETHACRYLATE

M. F. Shostakovskii, E. N. Prilezhaeva, V. M. Karavaeva, Vysokomol. soedin. **1**: No. 5, 781–783, 1959.

DETERMINATIONS have been made of the relative activity coefficients of vinylethylsulphide on copolymerization with styrene and methylmethacrylate and the monomer reactivity factors (Q and e) for this substance have been calculated.

The values of r_1 and r_2 obtained show that vinylethylsulphide has greater affinity for its radical than is observed in the case of vinyl ethers of the oxygen series. The negative value of e confirms the electron-donor nature of the sulphide group.

ACTION OF IONIZING RADIATION ON THE NATURAL HIGH POLYMERS – THE LIGNO-CARBOHYDRATE COMPLEX AND ITS COMPONENTS

A. S. Freidin, Yu. M. Malinskii, V. L. Karpov, Vysokomol. soedin. **1**: No. 5. 784–790, 1959.

A STUDY has been made of the action of ionizing radiation γ-rays of Co-60 on wood, on its carbohydrate fraction, on lignin preparations isolated with the aid of dioxane and mineral acids, and on standard cotton cellulose of a high degree of purity. All components of the lignocarbohydrate complex are subjected to destruction on radiolysis, but the greatest changes are undergone by the polysaccharides, among which the most easily destroyed is hemicellulose. The enhanced radiation stability of lignin may be explained by its aromatic structure. Concentrated acids bring about condensation of the radiolysis products of lignin with the formation of stable compounds. Oxidation of the wood and of its components takes place independently of the destruction and of the presence of atmospheric oxygen.

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* Vol. 1, No. 6, 1959*

INVESTIGATION OF RELAXATION PROCESSES IN CELLULOSE ESTER FILMS

B. N. Korostylev, P. V. Kozlov, Vysokomol. soedin. 1: No. 6, 793–798, 1959.

SIGNIFICANT improvement in the mechanical properties of thin triacetate films was observed on short thermal treatment at high temperatures.

It has been shown that the treatment is connected occurring relaxation processes in the films, leading to decrease in internal stresses and to increase in the molecular chain packing density of the film-forming substance.

ON HETEROCHAIN POLYAMIDES—XX. PREPARATION OF POLYAMIDES BY REACTION BETWEEN CARBON SUBOXIDE AND DIAMINES

V. V. Korshak, S. V. Rogozhin, V. I. Volkov, Vysokomol. soedin. 1: No. 6, 799–803, 1959.

A STUDY of the reaction between carbon suboxide and various bifunctional compounds shows that linear polymers are formed both in the case of glycols and biphenols as well as in the case of diamines. The results obtained indicated the fallibility of Van-Alphen's conclusion as to the structure of products of the reaction in the case of aromatic diamines. The molecular weights of the polyamides depend upon the ratio of the reagents and the conditions of the reaction. Infra-red spectra of the polyamides obtained by the reaction between carbon suboxide and diamines confirm their identity with polyamides obtained from diamines and diethylmalonate.

ON HETEROCHAIN POLYESTERS—XX. REACTION BETWEEN CARBON SUBOXIDE AND GLYCOLS AND BIPHENOLS

V. V. Korshak, S. V. Rogozhin, V. I. Volkov, Vysokomol. soedin. 1: No. 6, 804–808, 1959.

WITH the objective of finding new ways for the synthesis of high molecular compounds the reaction between carbon suboxide and glycols and dibasic phenols has been investigated. It has been shown that linear polyesters are easily formed, the molecular weight of the latter considerably exceeding that attained for the same type of polyesters prepared by the usual polycondensation methods.

As in the case of polyesters obtained by polycondensation of dicarboxylic acids with glycols, the molecular weight of these polyesters has been shown to depend also upon the ratio between the reagents. An explanation has been advanced for the cause of the stop in chain growth of the polyester during interaction of carbon suboxide with hydroxyl-containing compounds.

ON HETEROCHAIN POLYAMIDES—XXI. STRUCTURAL DEPENDENCES OF THE MELTING TEMPERATURE IN HOMOLOGOUS SERIES OF HETEROCHAIN POLYMERS

T. M. Frunze, V. V. Korshak, Vysokomol. soedin. 1: No. 6, 809–818, 1959.

THE problem of the relation between the melting temperature and the heterochain characteristic (ratio of the number of heteroatomic to the number of methylene groups) has

* English abstracts reprinted from Vysokomol soedin. 1: No. 6, 1959.

been examined in the series of aliphatic heterochain polyamides containing nitrogen and oxygen. These quantities have been shown to be linearly correlated, the dependence being quite definitely expressed for compounds of the same structure. With change in structure and hetero-bond arrangement only the slope of the corresponding lines on the diagram changes. All lines intersect at a single point lying in the region of the melting temperature of polyethylene.

QUANTITATIVE EVALUATION OF THE DEFORMABILITY OF VITRIFIED HIGH POLYMERS

E. E. Glukhov, Vysokomol. soedin. **1**: No. 6, 819–824, 1959.

In the paper an apparatus has been described for testing plastics under pure shear conditions, with automatic recording of the strain-time curves under load and after removal of the latter. A mathematical treatment of the test results has been proposed enabling one to calculate from the experimental data the deformation for any time interval at any stress. The dual character of the deformation process, wherein under the influence of stress deformation take place leading simultaneously to a strengthening and to a break down of the material, has been examined.

STUDIES ON ORGANOPHOSPHORUS POLYMERS—VIII. POLYESTERS OF PHOSPHONIC ACIDS AND SOME AROMATIC DIOXYCOMPOUNDS

V. V. Korshak, I. A. Gribova, M. A. Andreeva, Vysokomol. soedin. **1**: No. 6, 825–828, 1959.

Polyesters of methyl-, phenyl- and phenoxyphosphonic acids as well as of such aromatic dioxycompounds as hydroquinone, resorcinol, 4,4′-dioxy-diphenyl and 4,4′-dioxydiphenyl-2,2 propane have been synthesized by the polycondensation of dichloranhydrides of phosphonic acids and aromatic dioxycompounds. The polyesters of phosphonic acids and aromatic dioxycompounds are brittle solids, soluble in chloroform, dichloroethane and cresol.

The softening temperature of the polyester has been shown to depend upon the nature of the initial acid and upon the structure of the aromatic dioxy compound.

The polyesters of phenylphosphonic acid possess higher softening temperatures than polyesters of methyl and of phenoxyphosphonic acids. The incorporation of an unsymmetrical dioxycompounds into the polyester molecule lowers the softening temperature, the highest value belonging to polyesters of 4,4′-dioxydiphenyl.

DYNAMOMECHANICAL PROPERTIES OF POLYETHYLENE UNDER VIBRATION IN SHEAR

S. P. Kabin, Vysokomol. soedin. **1**: No. 6, 829–833, 1959.

In the paper the results are described of investigations on the velocity and amplitude attenuation constant at frequencies 1 and 2 mHz of waves in polyethylene of density $\rho = 0{\cdot}91$ g/cm³ in shear over the temperature range -30 to 70°C. Within this temperature range to velocity changes from $C_t = 1{\cdot}6 \times 10^5$ to $C_t = 0{\cdot}4 \times 10^5$ cm/sec. The attenuation constant at 2 mHz increases from $\alpha_t = 6$ l./cm at $t = -60$°C to $\alpha_t = 46$ l./cm at $t = 70$°C. The value of α_t is approximately proportional to the frequency. Based on previously published work and on the present results, the shear modulus, bulk compression modulus, the Poisson coefficient and the slope of mechanical losses for the waves in shear have been calculated. No relaxation losses were observed in the region of subzero temperatures. In the positive temperature region small losses of medium frequency relaxation may be discerned. Relaxation losses at subzero temperatures were shown to occur on bulk deformation of polyethylene. The Poisson coefficient μ of polyethylene changes in value from $\mu = 0{\cdot}34$ at $t = -60$°C to $\mu = 0{\cdot}48$ at $t = 70$°C.

ON HETEROCHAIN POLYESTERS – XXI. MIXED POLYESTERS ON THE BASIS OF DIATOMIC PHENOLS

V. V. Korshak, S. V. Vinogradova, Vysokomol. soedin. **1**: No. 6, 834–837, 1957.

MIXED polyesters of the systems; terephthalic acid-resorcinol-*p,p'*-dioxydiphenylpropane, *iso*phthalic acid-resorcinol-hydroquinone, and *iso*phthalic acid-hydroquinone-*p,p'*-dioxydiphenylpropane have been synthesized and investigated. The effect of the reagent structure on the physical properties of the polyesters has been discussed.

ON HETEROCHAIN POLYESTERS – XXII. MIXED POLYESTERS OF DIATOMIC PHENOLS

S. V. Vinogradova, V. V. Korshak, Vysokomol. soedin. **1**: No. 6, 839–841, 1959.

MIXED polyesters of the systems *p,p'*dioxydiphenylpropane-adipic-terephthalic acids, *p,p'*-dioxydiphenylpropane-sebacic-terephthalic acids and hydroquinonesebacic-terephthalic acids have been synthesized. The effect of the reagent structure on the physical properties of the polyesters has been discussed.

RELATION BETWEEN MOLECULAR WEIGHT AND INTRINSIC VISCOSITY OF SOLUTIONS OF POLY-*p-tret*-BUTYLPHENYLMETHACRYLATE FRACTIONS IN BROMOBENZENE AND CARBON TETRACHLORIDE

O. V. Kallistov, I. N. Shtennikova, Vysokomol. soedin. **1**: No. 6, 842–845, 1959.

A STUDY has been made of the dependence beetwen the molecular weight and the intrinsic vicosity of solutions of poly-*p-tret*-butylphenylmethacrylate fractions in bromobenzene and carbon tetrachloride. Viscosity measurements of the high molecular fractions were made at different velocity gradients with the aim of obtaining the intrinsic viscosity at infinitely slow flow $[\eta]_{q\to 0}$. The molecular weight $\overline{M}_w$ determined by the method of light scattering lead to the relation for the polymer in both solvents: $[\eta]_{q\to 0} = 4{\cdot}1 \times 10^{-4} \overline{M}_w^{0{\cdot}71}$.

ON THE STEREOSPECIFICITY OF POLYMERS AS A FUNCTION OF THE POLYMERIZATION CONDITIONS

T. M. Birshtein, O. B. Ptitsyn, Vysokomol. soedin. **1**: No. 6, 846–851, 1959.

IT has been shown that interaction between the nearest non-adjacent R-groups in polymers of the type $(\text{-CH}_2\text{-CHR-})_n$ should lead to depenaence of the probability of *iso*- or syndiotactic addition of the monomer unit to the end of a growing chain on the type of addition to the previous monomer unit. On this basis the fact has been explained of the formation of stereoblock polymers consisting of alternate *iso*- and syndiotactic sequences. The possibility has been examined of investigating the microtacticity of polymer chains by their properties in solutions, which, as the authors have shown, should depend upon the stereoisomerism.

INTERNAL ROTATION AND PHYSICAL PROPERTIES OF POLYMER CHAINS – XVII. CONFORMATION OF POLY*iso*BUTYLENE AND POLYDIMETHYLSILOXANE MOLECULES IN SOLUTION

T. M. Birshtein, O. B. Ptitsyn, E. A. Sokolova, Vysokomol. soedin. **1**: No. 6. 852–856, 1959.

THE equations for the sizes and dipole moments of polymer chains with symmetrical side groups (based, as approximation, on independent conformation of the monomer units) have been extended to the case of alternating valency angles. The result obtained have been com-

pared with experimental data on the dimensions of polyisobutylene and polydimethylsiloxane macromolecules in ideal solvents. It seems that in both cases quasifree rotation exists within the limits of the monomer units, the restriction of rotation in the chain being due to correlation between conformations of neighbouring units.

FLOW BIREFRINGENCE OF POLYBUTYLMETHACRYLATE SOLUTIONS

V. N. Tsvetkov, S. Ia. Lyubina, Vysokomol. soedin. **1**: No. 6, 856–862, 1959.

THE dynamic birefringence and intrinsic viscosity have been determined of a number of polybutylmethacrylate (PBMA) fractions (M from $0{\cdot}06\times10^6$ to $8{\cdot}5\times10^6$) in benzene and ethyl acetate. It has been found that the difference in polarizabilities of the statistical segment of PBMA $a_1 - a_2 = -14\times10^{-25}$ cm^3. In contrast to polymethylmethacrylate considerable hindering of rotation around the bonds is observed in the side chains of PBMA, which may be ascribed to the interaction of the large ester groups separated by a methylene group. The degree of straightening out p of the molecular coil of PBMA has been determined, the mean value of p for all fractions being 2·4.

ON THE ADDITIVITY OF COMPRESSION IN COPOLYMERIZATION

L. B. Sokolov, A. D. Abkin, Vysokomol. soedin. **1**: No. 6, 863–864, 1959.

IT has been shown that in the copolymerization of 2-ethoxyethyl-α-chloroacrylate and of glycol di-α-chloroacrylate with methylacrylate, methylmethacrylate and styrene compression of the system is not a linear function of the composition of the copolymer formed. On the basis of these as well as other data it has been inferrred that additivity of compression in copolymerization is not a general case.

FORMATION OF MACRORADICALS IN THE MECHANICAL DESTRUCTION OF VITRIFIED POLYMERS

P. Yu. Butiagin, A. A. Berlin, A. E. Kalmanson. L. A. Blyumenfel'd, Vysokomol. soedin. **1**: No. 6, 865–868, 1959.

THE mechanodestruction of inorganic (quartz) and organic (polystyrene, polyethylene) vitrified polymers has been studied by the method of electronic paramagnetic resonance (ER). The destruction was carried out in a vibration mill at low temperatures. ER spectra corresponding to organic macroradicals and to atoms with free valences on the quartz surface have been found in the disersion products. In the case of polystyrene the free radical concentration attains a value of $4\cdot\times10^{18}$/g and for quartz 2×10^{17}/g.

VULCANIZATION OF RUBBER IN THE PRESENCE OF N,N-DIETHYL-2-BENZOTHIAZYL-SULPHENAMIDE AS ACCELERATOR

B. A. Dogadkin, O. N. Beliatskaia, A. V. Dobromyslova, M. S. Feldshtein, Vysokomol. soedin. **1**: No. 6, 878–888, 1959.

THE vulcanization of rubber in the presence of N,N-diethyl-2-benzothiazylsulphenamide is characterized by an S-shaped curve with an initial induction period of reaction. The activation energy of sulphur addition in the intial period is 30 kcal/mole, in the main period 14 kcal/mole.

Oxygen and peroxides accelerate sulphur addition. No induction is noted in a pure oxygen medium. In the process of interaction with rubber N, N-diethyl-2-benzothiazylsulphenamide

is reduced to mercaptobenzothiazole and diethylamine, the rate of formation of captax showing a maximum, corresponding to the time of maximum rate of vulcanization.

A mechanism has been proposed for the accelerating effect of N,N-diethyl-2-benzothiazylsulphenamide, explaining the particular shape of the kinetic curves.

A STUDY OF THE RATE OF OXIDATION OF POLYSACCHARIDES IN AN HOMOGENEOUS MEDIUM

V. K. Buianova, A. A. Konkin, Vysokomol. soedin. 1: No. 6, 889–893, 1959.

The effect of the composition and structure of polysaccharides on the rate of their oxidative destruction in alkaline medium has been investigated. As objects of study cellulose, amylose, galaktan, laminarin, xylan and algic and pectic acids were taken.

The oxidation was carried out in an homogenous medium, oxygen serving as the oxidizing agent. The process was followed by viscosity measurements. The rate costant of the reactions was calculated and the activation energy determined. It has been shown that the chemical structure of the polysaccharides greatly influences the rate of their oxidative destruction.

INVESTIGATION INTO THE STABILITY TOWARDS HYDROLYSIS OF TITANIUM, TIN AND ALUMINUM TRIETHYLSILOXANE DERIVATIVES IN THE PROCESS OF POLYMER FORMATION

K. A. Andrianov, A. A. Zhdanov, Vysokomol. soedin. 1: No. 6, 894–899, 1959.

THE stability towards hydrolysis of *tris*-(triethylsiloxy)aluminum, *tetrakis*-(triethylsiloxy)tin and *tetrakis*-(triethylsiloxy) titanium has been studied and it has been shown that the most stable is *tetrakis*-(triethylsiloxy)titanium.

REACTIONS OF ORGANOMETAL COMPOUNDS WITH SALTS OF HEAVY METALS—III. REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH TITANIUM

I. I. Boldyreva, B. A. Dolgoplosk, V. A. Krol, Vysokomol. soedin. 1: No. 6, 900–906, 1959

A STUDY has been made of the products of reaction between organoaluminium compounds $Al(C_2H_5)_3$, $Al(C_2H_5)Cl_2$ and $Al(C_2H_5)Cl_2$ and the titanium halides $TiCl_4$ and $TiCl_3$ in an inert solvent in connection with the use of these systems as catalysts in the polymerization of butadiene and isoprene. On interaction between triethylaluminium and titanium tetrachloride $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, $AlCl_3$, $TiCl_3$ and $TiCl_2$ may be found among the products depending upon the initial ratio of the components. Aluminium chloride and, as was shown in our laboratory, ethylaluminium chloride are catalysts inducing polymerization according to the cationic type.

$TlCi_4$ has been found to be reduced only to Ti^{+3} by alkylaluminium halides. The precipitate formed in this case is the brown modification of $TiCl_3$. In the case of ethylaluminium dichloride the precipitate contains an almost equivalent amount of aluminium chloride.

The violet modification of $TiCl_3$ is also not reduced by alkylaluminium halides even at elevated temperatures. Triethylaluminium under the same conditions partially reduces $TiCl_3$ to $TiCl_2$.

Comparison of the rate of interaction between titanium tetrachloride and various organoaluminium compounds shown that the reactivity decreases in the series: $Al(C_2H_5)_3 > Al(C_2H_5)_2 > Al(C_2H_5)Cl_2$.

KINETICS AND MECHANISM OF THE POLYCONDENSATION OF α-AMINO ACID ESTERS AND PEPTIDES—X. INVESTIGATION OF THE CONSTITUTION OF THE PRODUCTS OF INTERACTION BETWEEN THE ETHYL ESTER OF *d,l*-ALANINE AND N-CARBOXY-*d,l*-ALANINE ANHYDRIDE

K. T. Poroshin, N. I. Prokhorova, Yu. I. Khurgin, Vysokomol. soedin. **1**: No. 6, 907–912, 1959.

THE interaction of N-carboxy-*d,l*-alanine anhydride and the ethyl ester of *d,l*-alanine has been studied over a relative concentration ([A]/[E]) range from 0·08 to 100. As a result of polycondensation of the anhydride induced by the ester peptides are formed. With excess ester ([A]/[E]) after all the anhydride has been consumed the reaction proceeds in accordance with the mechanism of α-amino acid ester polycondensation via carbamate formation. Special experiments have shown that this reaction is very slow for α-alanine derivatives and leads mainly to formation of diketopiperazines. In support of this increase in the [A]/[E] ratio is accompanied by decrease in diketopiperazine formation. For [A]/[E]>1 the reaction takes place according to the mechanism of polycondensation of N-carboxy-*d,l*-amino acid anhydrides.

ON THE MECHANISM OF THE REVERSION PHENOMENON IN VULCANIZATES—XXI. COMMUNICATION FROM SERIES ON GEL STRUCTURE

V. Ia. Gavrischuk, P. I. Zubov, Vysokomol. soedin. **1**: No. 6, 913–917, 1959.

BASED on a study of the physico-mechanical properties of unfilled chloroprene, natural rubber, butadienestyrene and sodium divinyl vulcanizates as a function of vulcanization time, it has been concluded that reversion of the strength properties of these systems is associated with disruption not only of intermolecular but of intramolecular polysulphide bonds.

A STUDY OF THE PROPERTIES OF THE COLOPYMERS OF ETHYLENE CLYCOL WITH TEREPHTHALIC AND SEBACIC ACIDS

P. V. Kozlov, E. F. Russkova, Vysokomol. soedin. **1**: No. 6, 918–924, 1959.

SOME physical, physico-chemical and mechanical properties of a number of copolymers of ethylene glycol with terephthalic and sebacic acids have been investigated. It has been shown that change in the properties in general does not obey a linear relation with respect to the chemical composition of the polymer.

A STUDY OF THE PROPERTIES OF MIXED GLYCOL ESTERS OF TEREPHTHALIC AND SEBACIC ACIDS AS A FUNCTION OF THE ACID RATIO

G. L. Slonimskii, V. V. Korshak, V. V. Golubev, N. A. Velikovskaia, Vysokomol. soedin. **1**: No. 6, 925–928, 1959.

A NUMBER of mixed polyesters of ethylene glycol with terephthalic and sebacic acids has been investigated. Change in the acid ratio in the intermediate composition region has been shown to lead to polymers incapable of crystallization and possession exceptionally high elastic properties.

Transition of the crystalline form characteristic of polyethylene terephthalate to that characteristic of polyethylene sebacate takes place through a peculiar staggered change in phase state, via the amorphous state.

In the region of compositions where the one or the other crystalline state is preserved, gradual development of the amorphous state takes place with increasing content of molecular chains of the units of the other structure. At the same time properties of amorphous polymers are strikingly manifested within the framework of the crystalline state.

NEW METHOD OF POLYESTER SYNTHESIS

E. N. Zil'berman, N. M. Tepliakov, Vysokomol. soedin. 1: No. 6, 934, 1959.

DICHLORIDES of acid diimonium chlorides are obtained on reaction in the cold of aliphatic dinitriles with hydrogen chloride in organic solvents. Subsequent treatment with glycols leads to the formation of the hitherto unknown hydrochlorides of polyimino esters. On hydrolysis of the latter there are produced polyesters with nitrile and hydroxyl end groups. By this method polybutyleneadipate with m. p. 46·5° and molecular weight about 1000 has been synthesized.

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PAPERS TO BE PUBLISHED IN FULL ENGLISH TRANSLATION IN *POLYMER SCIENCE: U.S.S.R.* Vol. 1, No. 3, 1960

V. V. KORSHAK, S. L. SOSIN and M. V. CHISTIAKOVA: Preparation of high molecular compounds by the polyrecombination reaction.

O. B. PTITSYN and IU. E. EIZNER: Hydrodynamics of polymer solutions—III. Influence of volume effects on light scattering and the friction coefficient of macromolecules in solution.

V. V. KORSHAK, K. K. MOZGOVA and V. P. LAVRISHEV: Effect of low molecular compounds on the photochemical decomposition of the polyamide Anide G-669.

N. M. BAZHENOV, M. V. VOL'KENSHTEIN, A. I. KOL'TSOV and A. S. KHACHATUROV: Nuclear magnetic resonance studies—I. On polymers.

M. V. VOL'KENSHTEIN and IU. IA. GOTLIB: On the entropy elasticity of a continuous incompressible medium containing rigid anisotropic particles.

S. E. BRESLER, M. M. KOTON, A. T. OS'MINSKAIA, A. G. POPOV and M. N. SAVITSKAIA: Increasing the thermal stability of polymers by cyclization in macromolecular chains during their partial decomposition.

T. M. BIRSHTEIN and YE. A. SOKOLOVA: Internal rotation in polymer chains and their physical properties—XVIII. Mean optical anisotropy of isotactic polystyrene molecules.

V. N. NIKITIN, L. A. VOLKOVA, N. V. MIKHAILOVA and IU. G. BAKLAGINA: Concerning two crystalline modifications of 1,4-*trans*-polybutadiene.

G. L. SLONIMSKII and P. V. KOZLOV: The VIII Mendeleyev Congress and polymer science in the USSR.

YE. P. TEPENITSYNA, M. I. FAVEROV, A. M. KUT'IN and G. S. LEVSKAIA: Some investigations in the field of ethylene polymerization in the presence of complex organo-metallic catalysts.

V. V. KORSHAK, K. K. MOZGOVA and V. P. LAVRISCHEV: The influence of low-molecular-weight organic compounds on the ε-polycapramide photochemical destruction progress.

V. V. KORSHAK, K. K. MOZGOVA and V. P. LAVRISCHEV: The influence of low-molecular-weight compounds on the photochemical destruction of the polyamide Anide G-669.

A. T. KORITSKII, IU. N. MOLIN, V. N. SHAMSHEV, N. IA. BUBEN and V. V. VOEVODSKII: An electronic paramagnetic resonance study on the radicals formed in fast electron irradiation of polyethylene.

O. B. PTITSYN and IU. E. EIZNER: Molecular interactions in polymer solutions—I. The influence of volume effects on the second virial coefficient.

A. G. POSAMANTIR, A. A. KOROTKOV and I. S. LISHANSKII: Polymerization of olefines by catalyst complexes—I. Interaction of alkylaluminium chlorides and triethylaluminium with titanium tetrachloride.

A. L. KLEBANSKII and V. F. VOSIK: An investigation of the reactivity towards free radicals of model compounds of synthetic rubber—I. Interaction with the tertiary butyl radical.

A. L. KLEBANSKI and V. F. VOSIK: An investigation of the reactivity towards free radicals of mole compounds of synthetic rubbers—II. Interaction with diphenylpicrylhydrazyl.

IU. S. SPIRIN, A. R. GANTMAKHER and S. S. MEDVEDEV: The mechanism of polymerization in the presence of the organic compounds of alkali metals.

A. A. KOROTKOV, C. P. MITSENGENDLER, V. N. KRASULINA and L. A. VOLKOVA: Synthesis of poly-methyl methacrylate with regular microstructure.

E. B. LUDVIG, A. R. GANTMAKHER and S. S. MEDVEDEV: Characteristics of the mechanism of cationic polymerization—I. Copolymerization of the system—methylstyrene-styrene, *iso*butylene-styrene and vinyl *n*-butyl ether-styrene.

E. B. LUDVIG, A. R. GANTMAKHER and S. S. MEDVEDEV: Characteristics of the mechanism of cationic polymerization—II. On the mechanism of the elementary reactions of cationic polymerization.

S. E. BRESLER, E. N. KAZBEKOV and E. M. SAMINSKII: Macroradical studies in polymerization and degradation processes—II.

K. A. ANDRIANOV and N. M. NOVIKOV: Polymethylbutoxyphosphinealumoxanes.

V. S. ETLIS, K. S. MINSKER, E. E. RYLOV and D. N. BORT: Crystalline polyvinyl chloride.

E. M. SAVITSKAIA, L. F. IAKHONTOVA and B. P. BRUNS: Mechanism of ion exchange on carboxyl cation exchangers.

Abstracts of papers not published in full.

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PREPARATION OF HIGH MOLECULAR COMPOUNDS BY THE POLYRECOMBINATION REACTION*

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(*Received* 27 *May* 1958)

VOL. 1 1960

IT is well established that dimers are formed from solvent molecules when sources of free radicals are decomposed in the solvents [1–7]. Dimers are formed by recombination of secondary radicals, which arise by homolytic breaking of the weakest bond (most frequently a C–H bond) in the solvent molecule on reaction with active free radicals. If these dimers contain reactive tertiary and secondary hydrogen atoms they will be attacked by the free radicals leading to the formation of more complicated condensation products (trimers, tetramers etc.) called polymers or "dehydropolymers" [7]. Thus on irradiating acetyl peroxide in ethylbenzene [3] the tetramer $CH_3(C_6H_5)CH[C(C_6H_5)CH_3]_2CH(C_6H_5)CH_3$ was found together with the dimer (2,3-diphenylbutane); on reaction of the tertiary-butoxy radical with totuene, the trimer—1,2,3-triphenylpropane was obtained as well as dibenzyl [7]; trimers and tetramers were obtained together with the dimer by reacting diacetyl peroxide with aliphatic ketones [2]. Dimerization of cumene led to the formation of 2,3-dimethyl-2,3-diphenylbutane, which had neither secondary nor tertiary hydrogen atoms on α-carbon atoms and therefore was unable to form more complicated condensation products [3,7].

The present work shows attempts to use the reactions of the free radicals in solution to obtain high molecular compounds of linear structure starting from various inactive compounds. In distinction from reported investigations on free-radical reactions in the liquid phase, the following conditions were fulfilled in the present work; (1) compounds with two symmetrical substituent "active centres" (mainly alkyl groups) were chosen as solvents, since it might be practicable to increase the chain; (2) peroxides or other sources of free radicals were introduced into the reaction in not less than equal molecular amounts relative to the solvent.

p-Di*iso*propylbenzene was chosen as the model compound, the reaction of which has not been investigated with free radicals in the liquid phase. Various peroxides served as a source of free radicals, mainly *tert.*-butyl peroxide, since it

* Vysokomol. soedin. 1: No. 7, 937–945, 1959.

is a compound which is convenient to make and has been sufficiently studied in regard to mechanism of irradiation [8] and reactivity towards hydrocarbons of different types and structures.

As a result of reaction with *tert.*-butoxyl and methyl radicals, resulting from thermal decomposition of *tert.*-butyl peroxide in solution in *p*-diisopropylbenzene

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$
$$(CH_3)_3CO\cdot \rightarrow \cdot CH_3 + (CH_3)_2CO,$$

at 170–220° C, the hydrocarbon was converted into three types of product: (a) low molecular condensation products embodying a mixture of dimers and trimers, (b) benzene-soluble high-molecular products (linear polymers) with molecular weights up to 10000 (60 links or residues);

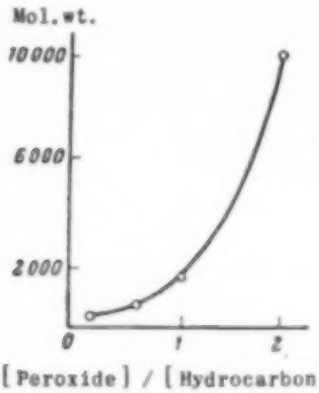


FIG. 1. Dependence of the molecular weight of the benzene soluble product of the polyrecombination of *p*-di*iso*propylbenzene on the molar ratio of peroxide: hydrocarbon.

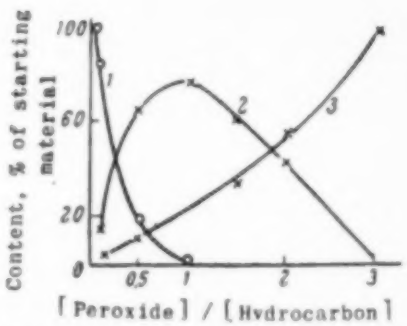


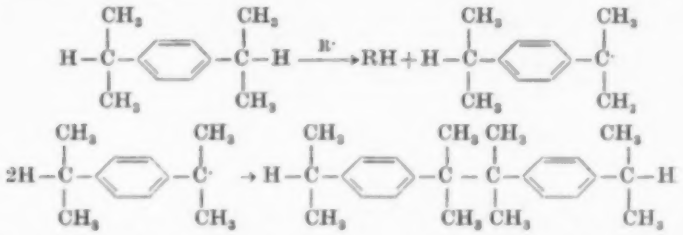
FIG. 2. Composition of reaction products in dependence on the molar ratio of peroxide: hydrocarbon (1) *p*-di*iso*propylbenzene; (2) low-molecular, (3) high-molecular reaction products.

(c) polymeric products insoluble in benzene and other common organic solvents; evidently possessing a net-like three dimensional structure. The benzene soluble and insoluble fractions were obtained as white powders, inert to acids, alkalies and oxidising agents, with a maximum melting point of 210–230°C for the soluble polymer; the insoluble polymer decomposed at 290–320°. X-ray investigation showed that the degree of crystallinity of the soluble polymer was about 10% and of the insoluble about 60%. The change in molecular weight of the soluble polymer depending on the molar ratio of peroxide: hydrocarbon is shown in Fig. 1, from which it is seen that a rapid increase in molecular weight begins after dissolving one mole of peroxide in one mole of hydrocarbon. This phenomenum is explained by the fact that the initial stage of the reaction is the result of converting the hydrocarbon into a mixture of the low-molecular products (Fig. 2). Thus, the second

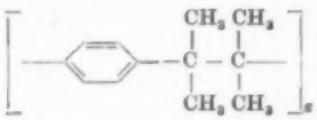
mole of peroxide begins to react not with the initial hydrocarbon but with the product of approximately treble molecular weight which leads to a more rapid growth of molecular weight in this stage of the reaction.

DISCUSSION OF RESULTS

The polymer chain growth process may be represented as a result of radical reactions in the following form:



and so forth, with the formation of polymers with the general formula.



In this way, the polymer is formed as a result of repeated acts of recombination of radicals of secondary origin (in the given case of hydrocarbons), therefore these reactions may be called polyrecombination reactions. As a sythetic method for high-molecular compounds, polyrecombination reactions differ principally from polymerisation reactions (starting materials are unsaturated compounds, radical reactions, but not chains). They possess certain characters formulated by Korshak [10] as indicators of polycondensation reactions [stepped character of the increase in molecular weight, isolation of low-molecular products e.g. *tert.*-butanol], but at the same time the polyrecombination reaction differs from polycondensation in the absence of the reverse process, chain destruction of the high polymer. The formation of insoluble polymers may be explained by abstraction of hydrogen by *tert.*-butoxyl or methyl radicals from the methyl group of a long chain molecule and knitting together of the latter to form a three dimensional structure. According to the data of Kharasch [3] and Farmer [7], the dimer of cumene is stable to the influence of free radicals since tertiary and secondary hydrogen atoms are absent from this molecule. However in the work of these authors only a negligible conversion of the hydrocarbon to dimer took place because they took it in excess in relation to peroxide which therefore reacts in the first place with the hydrocarbon. In our conditions with an excess of peroxide and consequently with higher conversion and higher concentration of polydi*iso*propylbenzene in the reaction mixture, the possibility of attack on methyl groups of the po-

lymer chain by active radicals is more likely than the abstraction of tertiary hydrogen atoms from end groups. In connection with this, as can be seen from Fig. 3, insoluble polymers are formed in larger quantity than the soluble polymers. Especially important in the formation of the three dimensional structure is the selec-

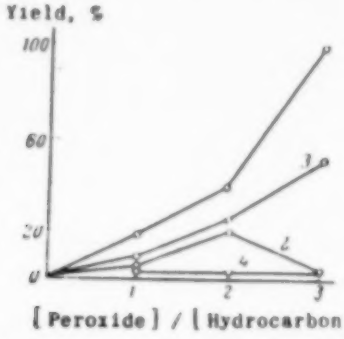
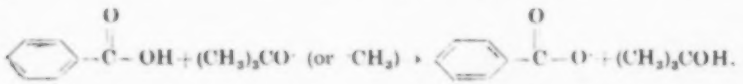


Fig. 3. Influence of benzoic acid on the yield of soluble and insoluble reaction products. (1) insoluble, (2) soluble products (benzoic acid absent); (3) soluble, (4) insoluble products (benzoic acid present).

tive influence of the primary free radical on the different parts of the polymer chain. Such selectivity is shown for example by the benzoyl radical. On decomposition in *p*-di*iso*propylbenzene of benzoyl peroxide, introduced in the ratio 2 moles per mole of hydrocarbon a polymer is obtained which is completely soluble in benzene and has a M. wt. of 2000, which corresponds to a degree of polymerisation of 12. This fact was successfully used for the considerable decrease of the insoluble part of the polymer which is obtained on reaction of *p*-di*iso*propylbenzene with *tert.*-butyl peroxide. It was found that if this reaction was carried out in the presence of benzoic acid (0·5 mole to 1 mole of hydrocarbon with the retention of all the rest of the conditions) then we obtained the linear polymer almost exclusively, though with a lower molecular weight (about 3000). The ratio of linear to three dimensional polymer obtained in the presence and absence of benzoic acid is shown in Fig. 3. Benzoic acid was isolated unchanged from the products of reaction; evidently in the given case benzoic acid is a modifier of the process, generating benzoate radicals which lead to the formation of linear polymers only, as has been shown in the case of benzoyl peroxide.

The generation of benzoate radicals may be represented in the following way



The fact that on change of benzoic acid to methyl benzoate the modifying influence vanishes and again the insoluble polymer is formed predominantly, serves to confirm this mechanism.

TABLE 1. DECOMPOSITION OF *TERT.*-BUTYL PEROXIDE IN *P*-DI*ISO*PROPYLBENZENE AT 200°

	Benzoic acids absent					50% Benzoic acid present					
Molar ratio of peroxide:hydrocarbon	1:0·1	1:0·5	1:1	1:2	1:3	1:1*	1:2*	1:3*	1:1	1:2	1:3
Unchanged hydrocarbon, % of starting material	85	16·8	0	0	0	0	0	0	0	0	0
Yield of methanol-soluble low-molecular product (%)	14·4	65·5	78	41	0	93·7	74	40·6	93·2	76·2	31·2
Yield of benzene-soluble polymer (%)	1·2	5·0	6·2	20	0	6·3	26·2	59	6·8	23·8	48·8
Yield of benzene-insoluble polymer (%)	0	12·5	15·5	39	100	No insoluble products					
General yield of high-molecular products, % of starting materials	1·2	17·5	22	59	100	6·3	26·2	59	6·8	23·8	48·8
Content yield of high-molecular products, as % of total high-molecular products	100	35	30	29	0	100	100	100	100	100	100
Molecular weight of benzene soluble polymer	500	750	1700	10000	—	650	1500	1750	800	3000	3300
M. pt. of benzene soluble polymer (°C)	210–230	190–210	195–210	190–250	—	148–159	139–146	145–155	150–160	152–162	145–160

* Reaction carried out at 170°

TABLE 2. DECOMPOSITION OF BENZOYLPEROXIDE IN *P*-DI*ISO*PROPYLBENZENE

Molar ratio of peroxide to hydrocarbon	1:16·5	1:2	1:1	2:1
Experimental temperature (°C)	140	140	140	140
		1000	1600	2000
Molecular weight of polymer obtained* m.pt. (°C)		136–150	140–155	146–150

* In all experiments only benzene-soluble polymers were obtained.

TABLE 3. DECOMPOSITION OF PEROXIDE IN VARIOUS COMPOUNDS

Solvent	Diphenyl	*p*-Xylene	Di*iso*propyl-ketone	Di*iso*propyl-ferrocene	*p*-Dichloro-benzene
Peroxide	*tert.*-Butyl	Benzoyl	Benzoyl	*tert.*-Butyl	*tert.*-Butyl
Molar ratio of peroxide to hydrocarbon	1:1	1:1	1:1	1:1	1:1
Experimental temperature (°C)	200	130	130	170	170
Mol. wt. of soluble polymer	1500	1600	800	8200	3000
M.pt. of polymer(°C)	136–166	108–130	172–183	155–180	230–280
Outward appearance	White powder	Yellowish powder	White powder	Reddish powder	Yellow powder
Solubility *					
in benzene	p	p	p	p	p
in chloroform	p	p	p	p	p
in methylethylketone	p	p	p	h.p.	h.p.
in ether	h.p.	h.p.	h.p.	h.p.	h.p.
in methanol	h.p.	h.p.	h.p.	h.p.	h.p.
Found (%)					
C	92·82	92·77	74·65	71·21	—
H	7·15	7·15	6·45	7·14	—
Fe	—	—	—	20·56	—
Cl	—	—	—	—	35·12
Basic group	C_6H_4	C_6H_6	$C_7H_{12}O$	$C_{16}H_{22}Fe$	C_6H_3Cl
Calculated (%)					
C	94·73	92·25	75·00	71·11	—
H	5·27	7·75	10·71	8·14	—
Fe	—	—		20·74	—
Cl	—	—	—	—	32·12

* p = soluble; h.p. = insoluble

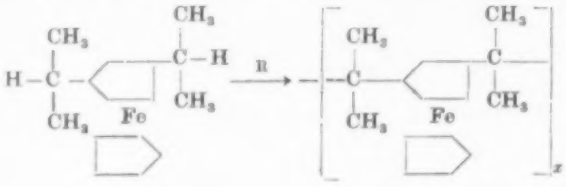
Analysis of the benzene soluble polydi*iso*propyl-benzene obtained with benzoyl peroxide, and in the presence of benzoic acid, showed that oxygen was contained in the polymer, due to the presence of benzoate radicals as end groups. The structure of the polymer with molecular weight 1000 may be expressed by the formula

$$C_6H_5COO\left[C(CH_3)_2C(CH_3)_2\text{-}C_6H_4\text{-}\right]_x OOCC_6H_5 .$$

The introduction of benzoate radicals into solvent molecules was ascertained by Gelissen and Hermans [14] by decomposing benzoyl peroxide in benzene diphenyl and *ter*-phenyl, and by Bagdasaryan and Miliutinskaya [15] by decomposing it in benzene.

The results of experiments on the decomposition of peroxides in *p*-di*iso*propylbenzene are presented in Tables 1 and 2.

The use of the polyrecombination reaction under the same conditions was studied by us on a series of other compounds. Results of these experiments are presented in Table 3. From this data it is seen that a series of saturated compounds of various classes and structures may be converted into polymers by using the polyrecombination reaction. This reaction was also shown to be useful for obtaining polymers of a new type, metalo-organic, for example, polydi*iso*propylferrocene, formed from di*iso*propylferrocene by the reaction



EXPERIMENTAL SECTION

p-Di*iso*propylbenzene was distilled in vacuum over metallic sodium, b.p. 119–120°/50 mm; n_D^{20} 1·4906. Literature data: b.p. 120°/50 mm [11]; n_D^{20} 1·4898 [12]. Benzoyl peroxide was reprecipitated with methanol from a chloroform solution and was dried in vacuum. *Tert.*-butyl peroxide was distilled in vacuum; d_4^{20} 0·7951; n_D^{20} 1·3896. Literature data: d_4^{20} 0·7940, $n\ 2_D^{20}$ 1·390[13].

METHOD OF CONDUCTING EXPERIMENTS AND WORKING UP THE PRODUCTS OBTAINED

Conical four-necked flasks provided with a stirrer and a capillary funnel, (the end of which was drawn down almost into two flasks) a nitrogen inlet tube, and a condenser with a straight cooler and a trap for volatile reaction products, were used for the reactions. The reactions were carried out in the following way. The compound was placed in the flask and heated to the required temperature in a nitrogen atmosphere and the peroxide was added to the stirred mixture at a rate

of 5–6 ml/hr, while the butanol formed was distilled off. At the end of the reaction stirring was continued for 30 min, and then benzene was added to the reaction mixture and the insoluble part filtered off; the soluble product was twice precipitated from benzene solution with methanol. The latter was distilled off and unreacted hydrocarbon or other starting material distilled from the residue in vacuum. The residue after redistillation in vacuum contained low molecular reaction products soluble in methanol.

For characterisation of the products the molecular weight (cryoscopic or ebullioscopic) and melting point in a capillary were determined. The volatile reaction products from the receiver and trap were combined and fractionally redistilled. The distillate from the reaction of di*iso*propylbenzene with *tert.*-butyl peroxide at 200°C was approximately half acetone (b.p. 54–57°C) and *tert.*-butanol (b.p. 80–83; n_D^{20} 1·3869). A series of experiments on the interaction of *p*-di*iso*propylbenzene with *tert.*-butyl peroxide were carried out by this experimental method and polymeric products obtained, part of which were soluble in benzene and part insoluble. The ratio of the first part to the second depended on the quantity of *tert.*-butyl peroxide added (Table 1). The benzene soluble reaction product was a white powder with m.p.190–230°C, stable to mineral acids, alkalies and oxidising agents. The polymer was partially soluble in chloroform but insoluble in methanol, ether, methyl ethyl ketone and cresol.

Found %: C 90·02; H 9·98
$C_{12}H_{16}$ Required %: C 89·93; H 10·07

It is evident from the elementary analysis given that the polymer does not contain oxygen.

Experiments on the decomposition of *tert.*-butyl peroxide in *p*-di*iso*propylbenzene in the presence of benzoic acid were carried out by the method described above; after the experiment benzoic acid was extracted with a soda solution. The polymers obtained in this way were slightly yellow powders with m.p. 145–160°C. The polymers were completely soluble in benzene, poorly soluble in chloroform and insoluble in methanol and ether.

Found %: C 87·93; H 9·62
$C_{12}H_{16}$ Required %: C 89·93; H 10·07

The polymers contained oxygen.

Decomposition of tert-butyl peroxide in p-diisopropylbenzene in the presence of methylbenzoate. Starting materials were 16 g *p*-di*iso*propylbenzene (1·0 mole), 14·5 g *tert.*-butyl peroxide (0·1 mole) and 7 g methyl benzoate (0·05 mole). As a result of the reaction 12·2 g low-molecular products (76·2% of starting material), 1·8 g benzene soluble material (11·3% of starting material) and 2 g insoluble products (53·6% of the total high-molecular products) were obtained. The molecular weight of the soluble part was 800.

The reaction of p-diisopropylbenzene with benzoyl peroxide was carried out as follows : the peroxide was placed in an ampoule and gradually added to the reaction

mixture by shaking; at the end of the reaction, the reaction products were dissolved in benzene and the benzoic acid, formed by the breakdown of benzoyl peroxide, was extracted with soda solution. The polymeric products were twice precipitated from benzene solution with methanol. The polymers obtained in this way were yellowish powders with m.p. 140–150°C (Table 2), readily soluble in benzene, poorly soluble in chloroform and insoluble in methanol and ether.

Found %: C 84·30; H 7·40

$(C_{14}H_{20}O_4)_n$ Required %: C 85·12; H 8·62

The reactions of peroxides with a series of other compounds besides *p*-di*iso*propylbenzene were carried out. The results are in Table 3.

SUMMARY

(1) It is shown that linear high molecular products can be synthesised from saturated compounds by a new method—the polyrecombination reaction based on the recombination reactions of solvent free radicals.

(2) The reaction was investigated with *p*-di*iso*propylbenzene as the example (linear polymers with molecular weights of ~ 10,000 were obtained) and extended to a series of other saturated compounds possessing reactive hydrogen atoms such as *p*-xylene, di*iso*propylketone, di*iso*propylferrocene, and also diphenyl and *p*-dichlorobenzene.

(3) In the polyrecombination reaction chain growth is accomplished by frequently repeated acts of formation and recombination of radicals, i.e. it is stepwise in character. In this way, and the isolation of low-molecular reaction products, it is similar to the polycondensation reaction. However, in distinction from the latter, the reverse process of chain destruction is apparently absent from the polyrecombination reaction.

(4) It is shown that it is possible to regulate the ratio of insoluble (three-dimensional) to soluble (linear) polymer in the reaction of *p*-di*iso*propylbenzene with *tert.*-butyl peroxide by adding benzoic acid to the reaction mixture as modifier, and a possible mechanism for its effect is discussed.

Translated by M. J. NEWLANDS

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HYDRODYNAMICS OF POLYMER SOLUTIONS—III. INFLUENCE OF VOLUME EFFECTS ON LIGHT SCATTERING AND THE FRICTION COEFFICIENT OF MACROMOLECULES IN SOLUTION*

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(*Received* 18 *December* 1958)

INTRODUCTION

IN pervious work [1,2,3] it has been shown that inter-molecular interaction of a distant type ("volume effect") influences the scattering of light in solutions of linear polymer molecules and their hydrodynamic properties. On transfer from an ideal (in which the volume effect is absent) to a non-ideal solvent, the dimensions of macromolecules increase anisotropically in such a way that the distance between groups which are far apart increases more rapidly than those groups which are relatively close together. In non-ideal solutions not only do the dimensions of the chain increase, but also the ratio between the dimensions and other physical properties.

As was shown in papers [1,2,3] the volume effect decreases asymmetric light scattering, the friction coefficient and the specific viscosity by comparison with the corresponding constants for molecules of the same size in an ideal solvent. In other words with a better solvent, i.e. with increased importance of the volume effect, the asymmetric light scattering the friction constant, and the specific viscosity increase less strongly than would be expected from the theory of Debye [4], Kirkwood and Riseman [5] (or Zimm [6]) which is applicable, strictly speaking, only to ideal solvents. This is because the physical constants indicated depend to a greater extent on the distance between comparatively close atoms in the chain than does the mean square of the radius of inertia which characterises the molecular dimensions [7].

The influence of the volume effect on light scattering and hydrodynamic properties of macromolecules in solution was considered in an approximate way in papers [1,2,3] on the basis of the equation (see also [8,9]):

$$\overline{r^2_{p,t}} = \alpha_0^2 \left| t-p \right|^{1+\varepsilon} a^2, \qquad (1)$$

* Vysokomol. soedin. **1**: No. 7, 966–977, 1959.

where $r_{p,t}$=distance between groups p and t on the main chain; a=effective length of the group, and $0 < \varepsilon \leqslant 0{\cdot}20$ and increases with improvement of the solvent. On account of this, the distribution of $r_{p,t}$ around the mean square value was assumed to be Gaussian. In papers [1 and 3], a theory of light scattering and frictional constant was proposed, having to do with ..e small volume effect cases, in which an exact value for $\overline{r^2_{p,t}}$ was used but the distribution function was assumed to be Gaussian as before. Different approximate methods were used in papers [10–13] again for the small volume effect cases (see below).

In the present article an exact theory is proposed for the influence of small volume effects on the light scattering and friction constant of macromolecules in solution, and the results of the exact and approximate theories are compared.

INFLUENCE OF THE VOLUME EFFECT ON LIGHT SCATTERING BY POLYMER PARTICLES

As is well-known, the angular distribution of the relative intensity of light dispersal has the form

$$P(\theta) = \frac{1}{N^2} \sum_{p,t=1}^{N} \left(\overline{\frac{\sin \mu r_{p,t}}{\mu r_{p,t}}} \right), \tag{2}$$

where θ=angle of dispersion; N=number of groups in the chain; $\mu=(4\pi/\lambda')\sin(\theta/2)$; λ'=wave-length of light entering the solution,

$$\left(\overline{\frac{\sin \mu r_{p,t}}{\mu r_{p,t}}} \right) = \frac{\int_0^\infty \frac{\sin \mu r_{p,t}}{\mu r_{p,t}} f(r_{p,t})\, r^2_{p,t} \cdot dr_{p,t}}{\int_0^\infty f(r_{p,t})\, r^2_{p,t} \cdot dr_{p,t}}, \tag{3}$$

$f(r_{p,t})$= distribution function for $r_{p,t}$.

In an ideal solvent the function $f(r_{p,t})$ is Gaussian:

$$f_0(r_{p,t}) = \left[\frac{3}{2\pi \overline{(r^2_{p,t})_0}} \right]^{3/2} e^{-\frac{3r^2_{p,t}}{2\,\overline{(r^2_{p,t})_0}}}, \tag{4}$$

where

$$\overline{(r^2_{p,t})_0} = |t-p| a^2. \tag{5}$$

Substitution of equations (3–5) into formula (2) leads to the known Debye function [4].

$$P(\theta) = \frac{2}{x_0} \left[e^{-x_0} - (1 - x_0) \right], \tag{6}$$

where

$$x_0 = \overline{R^2_0} \mu^2, \tag{7}$$

and
$$\overline{R_0^2} = \frac{1}{2N^2} \sum_{p,t=1}^{N} \overline{(r^2_{p,t})_0} = \frac{1}{6} Na^2. \tag{8}$$

(the zero subscipt refers to an ideal solvent). Substitution of equation (1) into equation (4) leads to the approximate theory of light dispersion of polymer solutions in good solvents which was developed earlier by one of us [1]. An analogous theory was later proposed by Benoit [9].

An exact expression for the function $f(r_{p,t})$ with a calculated volume effect (for cases where the latter is small) has the form [14]

$$f(r_{p,t}) = f_0(r_{p,t}) - \vartheta \sum_{i<j} w_{p,t}(i,j), \tag{9}$$

where ϑ-effective exclusion volume of a group, and $w_{p,t}(i,j)$ with the various mutual dispositions of i,j,p,t is expressed by the formulae

1. $i < j \leqslant p < t$ and $p < t \leqslant i < j$.

$$w_{p,t}(i,j) = \left(\frac{\alpha\gamma}{\pi^2}\right)^{3/2} e^{-\gamma r^2_{p,t}}.$$

3. $i \leqslant p < j < t$:

$$w_{p,t}(i,j) = \left[\frac{\beta\varepsilon\zeta}{\pi^2(\beta+\varepsilon+\zeta)}\right]^{3/2} e^{-\frac{(\beta+\varepsilon)\zeta}{\beta+\varepsilon+\zeta} r^2_{p,t}}$$

4. $p < i < t < j$:

$$w_{p,t}(i,j) = \left[\frac{\delta\varepsilon\zeta}{\pi^2(\delta+\varepsilon+\zeta)}\right]^{3/2} e^{-\frac{(\delta+\zeta)\varepsilon}{\delta+\varepsilon+\zeta} r^2_{p,t}}$$

5. $i < p < t < j$:

$$w_{p,t}(i,j) = \left[\frac{\gamma\varepsilon\zeta}{\pi^2(\varepsilon+\zeta)}\right]^{3/2} e^{-\frac{\varepsilon\gamma+\varepsilon\zeta+\gamma\zeta}{\varepsilon+\zeta} r^2_{p,t}} \tag{10}$$

6. $p < i < j < t$:

$$w_{p,t}(i,j) = \left[\frac{\alpha\varepsilon\zeta}{\pi^2(\varepsilon+\zeta)}\right]^{3/2} e^{-\frac{\varepsilon\zeta}{\varepsilon+\zeta} r^2_{p,t}}$$

where

$$\alpha = \frac{3}{2a^2|i-j|}, \quad \beta = \frac{3}{2a^2|p-j|}, \quad \gamma = \frac{3}{2a^2|p-t|}, \tag{11}$$
$$\delta = \frac{3}{2a^2|t-i|}, \quad \varepsilon = \frac{3}{2a^2|p-i|}, \quad \zeta = \frac{3}{2a^2|t-j|}.$$

Cases 1 and 2 correspond to the disposition of the interacting i and j within the "tails" of the chain, i.e. internal interaction within the tails (I and III in Fig. 1). Case 3 corresponds to interaction of the "middle" of the chain (II) with the "tail" (I); case 4—interaction of the "middle" with the "tail" (III); case 5 refers to the interaction of the "tails" and case 6 to internal interaction in the

"centre" of the chain. The last interactions play a major role. As was shown in paper [14], the increase of the mean square radius of inertia of the chain on account of the volume effect is mainly (up to 72 per cent) determined by interactions of this type.

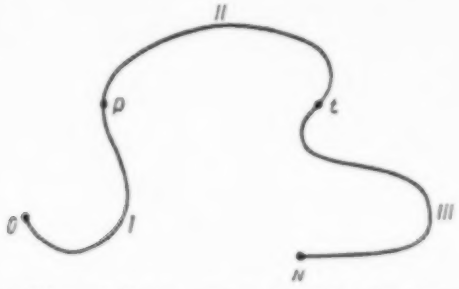

FIG. 1. Disposition of the groups p and t in the polymer chain.

By the substitution of equations (4), (5), (9), (10) and (11) into equation (3), we obtained a linear relation for ϑ within the limits of the article:

$$\left(\frac{\overline{\sin \mu r_{p,t}}}{\mu r_{p,t}}\right)=e^{-\frac{\mu^2 a^2}{6}|t-p|}\left[1-\left(\frac{3}{2\pi a^2}\right)^{3/2}\vartheta\sum_{i<j}\frac{\Delta_{ij}}{(j-i)^{3/2}}\right], \tag{12}$$

where

$$\begin{aligned}
&\Delta_{ij}^{(1)}=\Delta_{ij}^{(2)}=0;\\
&\Delta_{ij}^{(3)}=e^{\frac{\mu^2 a^2}{6}\frac{(j-p)^2}{j-i}}-1;\\
&\Delta_{ij}^{(4)}=e^{\frac{\mu^2 a^2}{6}\frac{(t-i)^2}{j-i}}-1;\\
&\Delta_{ij}^{(5)}=e^{\frac{\mu^2 a^2}{7}\frac{(t-p)^2}{j-i}}-1;\\
&\Delta_{ij}^{(6)}=e^{\frac{\mu^2 a^2}{6}(j-i)}-1.
\end{aligned} \tag{13}$$

Here the indices 1 to 6 of Δ_{ij} correspond to the numbers in equation (10). Substitution of equations (12) and (13) into equation (2), transformation of the summation into an integration and introduction of the new variables $u=p/N$, $w=t/N$, $\xi=i/N$, $\eta=j/N$, we get:

$$P(\theta)=\frac{2}{x_0^2}[e^{-x_0}-1+x_0]-2z\sum_{k=1}^{6}I_k. \tag{14}$$

where

$$z=\left(\frac{3}{2\pi a^2}\right)^{3/2}N^{1/2}\vartheta. \tag{15}$$

$$I_1=I_2=0;$$

$$I_3=\int_0^1 dw\int_0^w e^{x_0(w-u)}\,du\int_w^1 d\eta\int_0^u \frac{e^{x_0\frac{(\eta-u)^2}{\eta-\xi}}-1}{(\eta-\xi)^{3/2}}\,d\xi; \tag{16}$$

$$I_4=\int_0^1 dw\int_0^w e^{-x_0(w-u)}\,du\int_w^1 d\eta\int_u^w \frac{e^{x_0\frac{(w-\xi)^2}{\eta-\xi}}-1}{(\eta-\xi)^{3/2}}\,d\xi;$$

$$I_5=\int_0^1 dw\int_0^w e^{-x_0(w-u)}\,du\int_w^1 d\eta\int_0^u \frac{e^{x_0\frac{(w-u)^2}{\eta-\xi}}-1}{(\eta-\xi)^{3/2}}\,d\xi;$$

$$I_6=\int_0^1 dw\int_0^w e^{-x_0(w-u)}\,du\int_u^w d\eta\int_u^\eta \frac{e^{x_0(\eta-\xi)}-1}{(\eta-\xi)^{3/2}}\,d\xi.$$

The integrals I_3–I_6 cannot, generally speaking, be expressed by elementary functions. We shall represent it as a power series in x_0, which may give a good idea of the function $P(\theta)$ in the field of small θ (because $x_0 \sim \sin^2(\theta/2)$).

The appropriate calculations give:

$$P(\theta)=\frac{2}{x_0^2}[e^{-x_0}-(1-x_0)]-z\left\{\sum_{n=0}^{\infty}\frac{(-x_0)^{n+1}}{(n+5/2)(n+7/2)}\right\}. \tag{17}$$

$$\sum_{k=0}^{n}\frac{(-1)^{k+1}}{(k+1)!\,(k+3/2)^2\,(n-k)!}+\sum_{n=0}^{\infty}\frac{2^{n+4}\,(-x_0)^{n+1}}{(2n+7)!!}\sum_{k=0}^{n}\frac{22k+3}{2k+3}+$$

$$+\sum_{n=0}^{\infty}\frac{(-x_0)^{n+1}}{n+7/2}\sum_{k=0}^{n}\frac{(2k+2)!\,(-1)^k}{(k+1)!\,(k+3/2)}\sum_{m=0}^{2k+2}\frac{(-1)^m}{m!\,(m-k-1/2)(n+k+3-m)!}+$$

$$+\sum_{n=0}^{\infty}\frac{(-x_0)^{n+1}}{(n+5/2)(n+7/2)}\sum_{k=0}^{n}\frac{(-1)^{k+1}}{(k+1)!\,(n-k)!\,(n+k+3)(n+k+4)}+$$

$$+\sum_{n=0}^{\infty}\frac{(-x_0)^{n+1}}{(n+5/2)(n+7/2)}\sum_{k=0}^{n}\frac{(-1)^{k+1}}{(n-k)!\,(k+1)!\,(k+1/2)(k+3/2)}.$$

Calculation of some of the first members of the large series shown leads to the following equation for $P(\theta)$, which is correct for small θ:

$$P(\theta)=\frac{2}{x_0^2}[e^{-x_0}-(1-x_0)]\,z\left[\frac{134}{315}x_0-0{\cdot}1944\times x_0^2+\right.$$

$$\left.+0{\cdot}05438\times x_0^3-0{\cdot}01141x_0^4+0{\cdot}001890x_0^5-\ldots\right]. \tag{18}$$

An analogous result was recently obtained in a somewhat different form by Yamakawa and Kurata [15, 16].

Let us introduce

$$x = x_0\left(1+\frac{134}{105}z\right) = \overline{R^2}\mu^2, \tag{19}$$

where R^2—mean square radius of inertia of the chain with the calculated volume effect, which as is known from [17] [18], equals,

$$\overline{R^2} = \overline{R_0^2}\left(1+\frac{134}{105}z\right). \tag{20}$$

Then equation (18) takes the form

$$P(\theta) = \frac{2}{x^2}[e^{-x}-(1-x)]+z(-0{\cdot}01829\,x_0^2+0{\cdot}00943\,x_0^3- \\ -0{\cdot}00277\,x_0^4+0{\cdot}00064\,x_0^5-\ldots), \tag{21}$$

whence with $x \ll 1$

$$P^{-1}(\theta) = 1+\frac{x}{3}+\frac{x^2}{36}(1+0{\cdot}66z)+\ldots \tag{22}$$

Application of the Debye theory to a non-ideal solvent, i.e. equation (6) with the substitution of x_0 by x (i.e. $\overline{R_0^2}$ by $\overline{R^2}$) would give

$$P^{-1}(\theta) = 1+\frac{x}{3}+\frac{x^2}{36}+\ldots \tag{23}$$

Comparison of equations (22) and (23) shows that the initial slope of the curve $P^{-1}(\theta)$ is correctly given by the Debye theory, although the initial curvature in a non-ideal solvent is somewhat larger than appears from the Debye theory. However, from equations (21) and (22) it is seen that this effect should be very small and may be scarcely detectable in experiments (see also [16]).

Now consider the asymptotic behaviour of the function $P(\theta)$, expressed by equation (14), with $x_0 \gg 1$. We shall restrict the investigation to the integral I_6, which, as already shown, represents the major part of the interaction (internal interaction in the centre of the chain). Since the integral expression in I_6 depends on the different interchanges $w-u=\vartheta$ and $\eta-\xi=\zeta$, the integral I_6 may be written in the form

$$I_6 = \int_0^1 (1-\vartheta)e^{-x_0\vartheta}\,d\vartheta\int_0^{\vartheta}(\vartheta-\zeta)\frac{e^{x_0\zeta}-1}{\zeta^{1/2}}\,d\zeta. \tag{24}$$

Changing the order of integration and then integrating we obtain

$$I_6 = \left(\frac{1}{x_0^2}-\frac{2}{x_0^3}\right)\int_0^1\frac{1-e^{-x_0\zeta}}{\zeta^{1/2}}\,d\zeta+\left(\frac{1}{x_0^2}-\frac{2}{x_0^3}\right)e^{-x_0}\int_0^1\frac{e^{x_0\zeta}-1}{\zeta^{1/2}}\,d\zeta \\ -\frac{1}{x_0^2}\int_0^1\frac{1-e^{-x_0\zeta}}{\zeta^{1/2}}\,d\zeta-\frac{e^{-x_0}}{x_0^2}\int_0^1\frac{e^{x_0\zeta}-1}{\zeta^{1/2}}\,d\zeta. \tag{25}$$

The integrals in the right hand side of equation 25 take the following forms when $x_0 \gg 1$

$$\int_0^1 \frac{1-e^{-x_0\zeta}}{\zeta^{3/2}}\,d\zeta = x_0^{1/2}\int_0^\infty \frac{1-e^{-\chi}}{\chi^{3/2}}\,d\chi + O(1); \qquad e^{-x_0}\int_0^1 \frac{e^{x_0\zeta}-1}{\zeta^{3/2}}\,d\zeta = O\left(\frac{1}{x_0}\right); \tag{26}$$

$$\int_0^1 \frac{1-e^{-x_0\zeta}}{\zeta^{1/2}}\,d\zeta = O(1); \qquad e^{-x_0}\int_0^1 \frac{e^{x_0\zeta}-1}{\zeta^{1/2}}\,d\zeta = O\left(\frac{1}{x_0^{1/2}}\right).$$

It is easily seen that

$$\int_0^\infty \frac{1-e^{-x}}{\chi^{3/2}}\,d\chi = 2\Gamma(1/2) = 2\sqrt{\pi}. \tag{27}$$

Substituting equations (26) and (27) into equation (25) we get

$$I_6 = \frac{2\sqrt{\pi}}{x_0^{3/2}} + O\left(\frac{1}{x_0^3}\right). \tag{28}$$

Since, whatever the value of x, the integrals I_3, I_4, I_5 cannot exceed the integral I_6, which represents the major part of the interaction, we have

$$\sum_{k=1}^{6} I_k = \frac{A}{x_0^{3/2}} + O\left(\frac{1}{x_0^3}\right), \tag{29}$$

where $A > 2\sqrt{\pi} = 3{\cdot}54$.

From equations (14) and (29) we obtain, when $x_0 \gg 1$

$$P^{-1}(\theta) = \frac{1}{2} + \frac{x_0}{2}\left\{1 + z\left[\frac{A}{x_0^{1/2}} + O\left(\frac{1}{x_0}\right)\right]\right\}. \tag{30}$$

Consequently the initial slope S_0 and the asymptote S_∞ of the curve of the dependence of $P^{-1}(\theta)$ on $\mu^2 \sim \sin^2(\theta/2)$ equal

$$S_0 = \frac{\overline{R^1}}{3}; \qquad S_\infty = \frac{\overline{R_0^2}}{2}. \tag{31}$$

Thus

$$\frac{S_0}{S_\infty} = \frac{2}{3}\alpha^2, \tag{32}$$

where $\alpha^2 = R^2/R_0^2 = 1 + 134/105\,z$ . . . . . is the increase in dimensions of a macromolecule relative to the ideal solvent (see equation (21)).

We see that the initial slope of the dependence of P^{-1} on μ^2 is defined by the true dimensions of the chain in a non-ideal solvent, but the asymptote by the dimensions of the chain in an ideal solvent. A similar situation arises for branched chains where the initial slope is defined by the dimensions of the branched chain whereas the asymptote is defined by the dimensions of the linear chain with

the same molecular weight. This is explained by the fact that the factors which chiefly influence the distance between distant groups on the chain (volume effect and degree of branching) do not affect the asymptote of the curve of P^{-1} against $\sin^2(\theta/2)$ as is evident from the structure of equation (2) [1], [7].

Equations (31) and (32) show that with an equal initial slope the asymptote of the $P^{-1}(\theta)$ curve for a good solvent goes lower than the asymptote for a poor solvent. Comparison of this result with equations (22) and (23) leads to the inference that with equal chain dimensions (i.e. equal initial slope) the curve $P^{-1}(\theta)$ in a good solvent with smaller θ goes somewhat higher, and with a higher θ is noticeably lower than in a poor solvent.

Equation (32) was earlier obtained by our approximate method (see equation (46) paper [1]). By this it was shown that the size of S_0/S_x where $S_x = dP^{-1}/d\mu^2$, very slowly tends to $(^2/_3)x^2$ as $x \to \infty$. In the limit, but with very large x

$$\frac{S_0}{S_x} = \frac{2}{3}\,\Phi\left(\frac{R}{\lambda'}, z\right), \tag{33}$$

where

$$\Phi\left(\frac{R}{\lambda'}, z\right) = 1 + \frac{134}{105}\,z - \frac{2{\cdot}36}{x^{1/2}}\,z. \tag{34}$$

Thus, with real accessible values of x, not exceeding a few tens, the curve of the dependence of P^{-1} on μ^2 is already far from the asymptote and has a slope greater than asymptotic, i.e. it is turned downwards.

From equations (22) and (30) of the exact theory we also obtained equation (33), in which

$$\Phi\left(\frac{R}{\lambda'}, z\right) \cong 1 + \frac{134}{105}\,z - \frac{A}{2x^{1/2}}\,z. \tag{35}$$

An exact valuation of the magnitude of A requires calculation of the integrals I_3, I_4, I_5, which is difficult. The greater part of A, got from the integral I_6, is equal to 3·54.

INFLUENCE OF THE VOLUME EFFECT ON THE FRICTION CONSTANT OF MACROMOLECULES

The constant of flowing friction of the macromolecule with a flowing solvent which is connected with the coefficient of flowing diffusion and the sedimentation constant, has the form [20]

$$F = \frac{3\pi N^2 \eta_s}{\sum_{l>p} (1/r_{pl})} \tag{36}$$

For a Gaussian chain in an ideal solvent using equations (4) and (5), we obtain

$$F = P_\omega / 6^{1/2} (\overline{R_0^2})^{1/2} \eta_0, \tag{37}$$

where

$$P_0 = \frac{(3\pi)^{3/2}}{2^{5/2}} = 5{\cdot}11. \tag{38}$$

In general the analogous equation (with the substitution of $\overline{R_0^2}$ for $\overline{R_2}$) is used for non-ideal solutions which as discussed above is considered to be impossible to calculate correctly.

An exact expression for $\overline{(1/r_{p,t})}$ with the calculated volume effect (exact when the latter is small) was obtained by Yamakawa and Kurata's method [12], with an analogous account in [14]. In our notation this expression has the form

$$\left(\overline{\frac{1}{r_{pt}}}\right) = \left(\frac{6}{\pi}\right)^{1/2} \frac{1}{a} \left\{ \varphi_1(p,t) - \frac{z}{\sqrt{N}} \left[4 \sum_{s=1}^{\infty} \frac{C_s \cdot s}{(s+1/2)(s^2-1/4)} + \right.\right.$$

$$+ \sum_{s=1}^{\infty} \frac{C_s}{s+1/2} \sum_{q=0}^{2s} \frac{(-)^{q+1}}{s-q+1/2} \binom{2s}{q} (\varphi_2(p,t) + \varphi_3(p,t) +$$

$$\left.\left. + \sum_{s=1}^{\infty} \frac{C_s}{s^2-1/4} (\varphi_4(p,t) + \varphi_5(p,t) + \varphi_6(p,t)) \right] \right\}, \tag{39}$$

where $\binom{2s}{q}$ is the number of combinations of q from $2s$

$$C_s = \frac{(2s)!}{2^{2s}(s!)^2}, \tag{40}$$

$$\begin{aligned}
\varphi_1(p,t) &= (t-p)^{1/2}, \\
\varphi_2(p,t) &= (t-p)^{-s-1/2} p^q t^{s-q+1/2}, \quad \varphi_3(p,t) = (t-p)^{-s-1/2} p^{s+1/2}, \\
\varphi_3(p,t) &= (t-p)^{-s-1/2} (N-p)^{s-q+1/2} (N-t)^q, \quad \varphi_4(p,t) = (t-p)^{-s-1/2} (N-t)^{s+1/2}, \\
\varphi_4(p,t) &= N^{-s+1/2} (t-p)^{s-1/2}, \\
\varphi_5(p,t) &= -(N-p)^{-s+1/2} (t-p)^{s-1/2} \\
\varphi_6(p,t) &= -t^{-s+1/2} (t-p)^{s-1/2}.
\end{aligned} \tag{41}$$

Substituting equations (40) and (41) into equation (36), and substituting integrals for the summations and using the fact that

$$\int_1^N dt \int_0^{t-1} \varphi_2(p,t)\, dp = \int_1^N dt \int_0^{t-1} \varphi_3(p,t)\, dp, \tag{41A}$$

we obtain

$$S = \sum_{t=1}^{N} \sum_{p=0}^{t-1} \left(\frac{1}{r_{pt}}\right) = \frac{4}{3} \left(\frac{6}{\pi}\right)^{1/2} \frac{N^{1/2}}{a} \left\{ 1 - \frac{3}{2} z \left[\sum_{s=1}^{\infty} \frac{C_s}{s^2-1/4} \left(\frac{s}{s+1/2} - \frac{1}{2s+3} \right) - \right.\right.$$

$$\left.\left. - \sum_{s=1}^{\infty} \frac{C_s}{s+1/2} I_s \right] \right\} \tag{42}$$

where

$$I_s = \sum_{q=0}^{2s} \frac{(-)^{q+1}}{s-q+1/2} \binom{2s}{q} \int_0^1 dy \int_0^y (y-x)^{-s-1/2} [x^{s+1/2} - x^q y^{s-q+1/2}] dx$$

$$= \int_0^1 d\vartheta \int_0^{1-\vartheta} \left(\frac{u}{\vartheta}\right)^{-s-1/2} \left\{ \sum_{q=0}^{2s} \frac{(-)^{q+1}}{s-q+1/2} \binom{2s}{q} \left[1 - \left(1+\frac{u}{\vartheta}\right)^{s-q+1/2} \right] \right\} du. \qquad (43)$$

The separate parts of the integrals on the right hand side of equation (43) compensate each other as will be seen subsequently.

Using the fact that

$$\frac{1-\left(1+\frac{u}{\vartheta}\right)^{s-q+1/2}}{s-q+1/2} = -\int_0^{\frac{u}{\vartheta}} (1+\tau)^{s-q-1/2} d\tau, \qquad (43A)$$

and carrying out the summation we get

$$I_s = \int_0^1 d\vartheta \int_0^{1-\vartheta} \left(\frac{u}{\vartheta}\right)^{-s-1/2} du \int_0^{\frac{u}{\vartheta}} \tau^{2s} (1+\tau)^{-s-1/2} d\tau. \qquad (44)$$

Introducing the new variable $t=u/\vartheta$ in place of u, changing the order of integration and carrying out the integration by ϑ, we have

$$I_s = \frac{1}{2} \int_0^\infty \frac{t^{-s-1/2} dt}{(1+t)^2} \int_0^t \tau^{2s} (1+\tau)^{-s-1/2} d\tau. \qquad (45)$$

Let us now turn to the calculation of the series introduced into the right hand part of equation (42).

Numerical calculation gives

$$\sum_{s=1}^{15} \frac{C_s}{s^2-1/4} \left(\frac{s}{s+1/2} - \frac{1}{2s+3} \right) = 0{\cdot}446,$$

$$\sum_{s=16}^{\infty} \frac{C_s}{s^2-1/4} \left(\frac{s}{s+1/2} - \frac{1}{2s+3} \right) \cong \frac{2}{\sqrt{\pi}} \sum_{s=16}^{\infty} \frac{1}{s^{3/2}} = 0{\cdot}006. \qquad (46)$$

The integrals I_s where $s=1{\cdot}2$ and 3 are calculated directly: $I_1=0{\cdot}100$; $I_2=0{\cdot}046$; $I_3=0{\cdot}027$. The other integrals are estimated above.

$$I_s < \frac{1}{4_s}.$$

As the result of the numerical calculation we have

$$\sum_{s=1}^{3} \frac{C_s}{s+1/2} I_s = 0{\cdot}043,$$

$$\sum_{s=4}^{\infty} \frac{C_s}{2+1/2} I_s < \frac{1}{4\sqrt{\pi}} \sum_{s=4}^{\infty} \frac{4}{s^{3/2}} \cong 0{\cdot}014. \tag{47}$$

By substituting equations (46) and (47) into (42), we obtain

$$S = \frac{4}{3}\left(\frac{6}{\pi}\right)^{1/2} \frac{N^{3/2}}{a} [1 - (0{\cdot}603 \pm 0{\cdot}10)\, z]. \tag{48}$$

Equations (48) and (37) give;

$$F = P_0 \cdot 6^{3/2} (\overline{R_0^2})^{1/2}\, \eta_0 [1 + (0{\cdot}603 \pm 0{\cdot}010) z], \tag{49}$$

where P_0 is defined before in equation (38). Changing from $\overline{R_0^2}$ to $\overline{R^2}$ using equation (20), we finally obtain;

$$F = P \cdot 6^{3/2} (\overline{R^2})^{1/2}\, \eta_0, \tag{50}$$

where

$$P = P_0 [1 - (0{\cdot}035 \pm 0{\cdot}010)\, z]. \tag{51}$$

Equation (51) shows that the volume effect leads to some divergence from the proportionality between F and $(\overline{R^2})^{1/2}$, i.e. that P shows a slight dependence on z (i.e. on the type of solvent). An analogous result was obtained earlier by Peterlin [10,11] and ourselves [3] on the basis of approximate calculations of Yamakawa and Kurata [12,13]. It must be emphasized, however, that the known effect is extremely small, i.e. in practice one may consider the frictional constant to be proportional to the macromolecule dimensions.

The Peterlin equation [10,11] is based on approximate calculations of $\overline{(1/r_{p,t})}$, obtained from exact computation of $\overline{(1/r_{oN})}$ by substituting N by lt–pl in the latter. It may be represented in the form

$$P = P_0 (1 - 0{\cdot}31z). \tag{52}$$

In paper [3] we obtained an approximate equation for P, originating from an exact calculation of $\overline{r_{p,t}^2}$, but assuming the function $f(r_{p,t})$ to be Gaussian, (an analogous approximation is carried out in [1,2,3] and [13])

$$P = P_0 (1 - 0{\cdot}22z). \tag{53}$$

The difference between the approximate equation (53) and the exact equation (51) is connected with the fact that the volume effect leads not only to anisotropic swelling of the particle but also to a sharpening of the maximum of the distribution function for $r_{p,t}$ [21], [14]. As can be easily seen, the latter

effect leads to an increase on P which thus partially compensates for the decrease of P arising from the anisotropic swelling of the particle. Using for $r^2_{p,t}$ the approximate equation (1) and the function $f(r_{p,t})$ previously assumed Gaussian, we obtained [3]:

$$P = P_0(1 - \varepsilon/4), \tag{54}$$

whence, with small z,

$$P = P_0(1 - 0{\cdot}16\,z). \tag{55}$$

Finally, from the approximate calculation of $f(r_{p,t})$ put forward by one of us [14] it follows that

$$P = P_0(1 - 0{\cdot}10\,z). \tag{56}$$

We see that the approximate theory (in particular equations (55) and (56)) also leads to a weak dependence of P on z (slight in comparison with the dependence of $(\overline{R^2})^{1/2}$ on z) .The exact theory leads to a still weaker dependence. Thus the result obtained by us in paper[3]—that the friction constant of macromolecule is proportional to its dimensions within experimental error—is confirmed by the results of the exact theory.

THE INFLUENCE OF THE VOLUME EFFECT ON THE INTRINSIC VISCOSITY

The influence of the volume effect on the intrinsic viscosity $[\eta]$ was shown by us earlier [2,3] on the basis of the approximate equation (1). From the results of this work (which we do not consider to be restricted to small values of z) it follows that for $z \ll 1$ the Flory factor Φ in the equation

$$[\eta] = \Phi \cdot 6^{3/2} \frac{(\overline{R^2})^{3/2}}{M} \tag{57}$$

(M=molecular weight) depends on z in the following way

$$\Phi \cong 2{\cdot}86 \times 10^{23}(1 - 1{\cdot}75\,z). \tag{58}$$

Comparison of equation (58) with the approximate equation (55) (obtained in a similar way) shows that the influence of the volume effect on Φ is greater than its influence on P.

Equation (58) allows for the influence of an isotropic chain swelling on the hydrodynamic interaction of segments of the molecule. The influence of anisotropic swelling on the distribution of segments relative to the centre of gravity is negligibly small. The latter circumstance is proved in paper [3], by partial solution of the integral equation of Kirkward and Riseman [5] with the exactly calculated influence of the volume effect on the segment distribution.

The influence of the volume effect on Φ was also shown recently in the papers of Yamakawa and Kurata [12,13]. The result the obtained has the form

$$\Phi = 3{\cdot}62 \times 10^{23}(1 - 0{\cdot}363\,z). \tag{59}$$

The coefficient of z in equation (59) is the sum of 0·141 and 0·222, which are connected with the influence of anisotropic chain swelling on segment distribution relative to the centre of gravity and on the hydrodynamic interaction of segments respectively. Thus Yamakawa and Kurata's result also shows that the influence of anisotropic swelling on segment distribution relative to the centre of gravity is small. At the same time the whole influence of the volume effect is comparatively small according to these authors. In connection with this it must be noted that the influence of anisotropic chain swelling on the hydrodynamic interaction of segments is considered in a very rough manner [12,13]. In addition Yamakawa and Kurata solved Kirkward and Riseman's integral equation by an incorrect method [22], originally used in [5], and not the strict method of Auer and Gardner [23] which we used. The method used by Yamakawa and Kurata gives $\Phi = 3{\cdot}62 \times 10^{23}$ when $z = 0$, in place of the correct value $\Phi = 2{\cdot}86 \times 10^{23}$ [24], [3]. As we showed in our calculation, the use of this method in our approximation, based on equation (1), would give the coefficient of z as 0·95 in equation (58) instead of 1·75.

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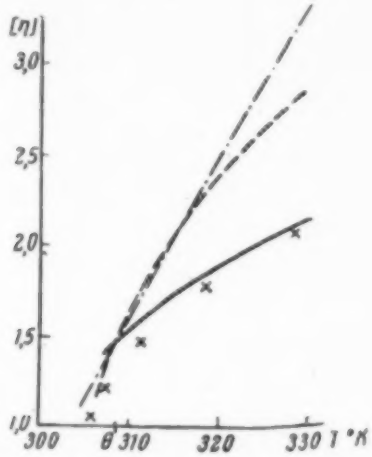

FIG. 2. Dependence of $[\eta]$ on temperature for a *cyclo*hexane solution of polystyrene. (x) Experimental data [25]; (— — —) Flory-Fox theory [26]; (— · — ·) Yamakawa-Kurata theory [12,13]; (————) Theory of authors [2,3].

It is necessary to emphasise that Yamakawa and Kurata's equation (59) is not capable of explaining the experimentally observed considerable increase of Φ with improvement of the solvent, which is quantitatively described by our theory [3]. Figure 2, in which are produced the experimental data on the dependence of $[\eta]$ on temperature for a *cyclo*hexane solution of polystyrene, and the theoretical dependence derived from the theory of Flory and Fox [26] (Φ = constant), Yamakawa and Kurata (equation (59)) and ourselves [2,3]. In

all cases $\Phi_0 = 2{\cdot}86 \times 10^{23}$ mole^{-1} (paper [13]). This value of Φ_θ was chosen to get agreement with experiments in ideal solvents ($T=\theta$).

A general form of equation (59) for the case of large z is put forward in [13] but comparison of this general equation with experiment has no physical meaning since equation (59) is essentially based on the assumption that z is small.

SUMMARY

From the above report it follows that the usual methods for defining the dimensions of macromolecules by $P(\theta)$, F and $[\eta]$, based respectively on equations (6), (50) (with $P=$const.) and (57) (with $\Phi=$const.) should strictly only be applied for poor solvents. For good solvents it is necessary to use our approximate theory for $P(\theta)$, F and $[\eta]$ proposed earlier [1,2,3] (exact equations (14) and (51) which were obtained in the present paper, apply only to those cases with small volume effects). The results of the present work, coupled with the results in [1–3], show that the volume effect scarcely influences the relation between F and $(\overline{R^2})^{1/2}$, so that equation (50) with $P=5{\cdot}11$ is correct in good solvents. On the other hand, the relation between $P(\theta)$ and $[\eta]$ on one side and $\overline{R^2}$ on the other is very noticeably distorted.* It is true that the initial slope of the curve $P^{-1}(\theta)$ gives us a value of $\overline{R^2}$ which is independent of any theory, but the measurement of the initial slope is practically impossible for very high molecular compounds.

The necessity for using the approximate theory, which allows for the volume effect for determining the dimensions of macromolecules from the viscosity and light dispersion in good solvents, of course reduces the reliability of results obtained in this way. However the use of this (present) theory is evidently in good quantitative agreement with experiment [3],[27], [28] and its use for the ends indicated seemed to be correct.

Translated by M. J. NEWLANDS

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EFFECT OF LOW MOLECULAR COMPOUNDS ON THE PHOTOCHEMICAL DECOMPOSITION OF THE POLYAMIDE ANIDE G-669*

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(*Received* 10 *March* 1959)

AS already reported earlier [1,2], two of us and Zasechkina have investigated the photochemical disintegration of polystyrene and polyethyleneterephthalate in the presence of added low molecular compounds.

In the present report results are presented on the influence of the addition of low molecular substances on the photochemical destruction of the mixed polyamide anide G-669 [3]. In contrast to the previous work in which samples of polymer film served as experimental objects, the results discussed in the present article were obtained with solutions of the polyamide in ethanol and in a mixture of the latter and dichloroethane.

It is known that polyamides, which have found wide practical usefulness in recent years, are insufficiently stable to the action of light, under the influence of which they lose their valuable properties comparatively quickly. Photochemical destruction of polyamides was more than once the object studied by investigators; it is sufficient to mention the papers of Achhammer [4] and other authors [5–20] who investigated the process of change of free polyamides under the action of light. In a series of reports, mainly patents, is published information about various stabilisers which are capable of retarding the process of photochemical destruction of polyamides [21–34]. However, we have not met literature data on the photochemical destruction of polyamides in solution up till now.

It is interesting to elucidate the influence of ultra-violet irradiation on polyamide solutions in some solvents and to observe the influence of stabilising additives on this. This is especially interesting for anide G-669, which has not been investigated from this point of view up till now. We used in our work additives which have been as yet little described – salol, β-methylumbelliferone, 2-(*o*-hydroxyphenyl)-benzoxazole, dixanthylene, and 2-hydroxynaphthaldazine. At first 2-hydroxybenzaldazine and *N*-monomethyltoluenesulphonamide were used. The

* Vysokomol. soedin. 1: No. 7, 990–997, 1959.

absorption spectra of the first five compounds were cited earlier [1]. The absorption spectra of the last two substances are shown in Fig. 1.

The objects of investigation was Anide G-669 with various molecular weights: 5000, 12500 and 23000, and in seperate experiments 17000. The absorption spectra of the initial polyamide and of its solutions in ethanol and in a mixture of the latter with dichloroethane are shown in Fig. 1.

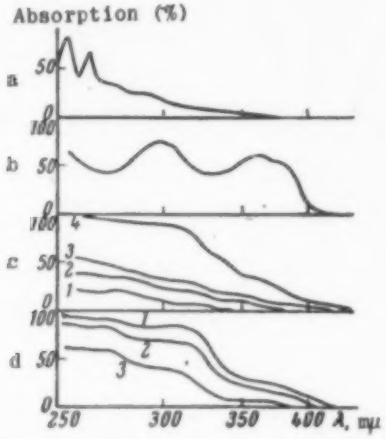

FIG. 1. Absorption spectra: (a) N-methyltoluenesulphamide; (*b*) 2-oxybenzaldazine; (*c*) solutions of anide G-669 (1) mol. wt. 5000; (2) 12,500; (3) 23,000; (4) 5000, 12,500, 23,000 after 50 hours irradiation; (*d*) solutions of anide G-669 after 50 hours irradiation. Additions: (1) β-methylumbellipherone; (2) salol; (3) N-methyltoluenesulphamide.

These particular solvents were chosen because they are sufficiently transparent for ultra-violet irradiations, are very stable to its action and dissolve the initial low-molecular compounds and polyamide well. Dichloroethane is slightly inferior to ethanol in stability to ultra-violet radiation—its viscosity is changed slightly and its absorption in the ultra-violet region of the spectrum is increased. After 50 hr irradiation it was found that the mixture of ethanol and dichloroethane had a specific viscosity of 0·05, but after this the viscosity of the mixture did not change with increased duration of irradiation. The low-molecular additives also did not alter the viscosity of the solvent in practice; in only one case was it increased by 0·01—after dissolving in it 0·4% 2-(*o*-hydroxyphenyl) benzoxazole. The change in properties of the solvent were immaterial, and permitted us to use the solvents for the purposes of the present investigation. Firstly a solution of the organic additives in known weights of solvent were prepared, to which were then added polyamide solutions. The solutions were irradiated with ultra-violet radiation, a PRK-2 lamp serving as source. A control solution of polyamide without any additive was irradiated simultaneously. Viscometry served as the basic met-

hod for investigating the change in properties of the polyamide by irradiation. In many experiments the change in optical properties of the solvent was studied, in particular its absorption spectrum in the ultraviolet region.

EXPERIMENTAL PART

For the experiments 0·005% solutions of the low molecular compounds in ethanol and a mixture of the latter with dichloroethane (2:1) were used. Anide G-669 was dissolved in them: the polyamide solution concentration was 0·5%. The solutions were poured into quartz viscometers with thin reservoirs (Fig. 2).

To exclude the entry of air and evaporation of the solvent in the irradiation process both ends of the viscometer were connected with a rubber tube. For the radiation an assembly was used which has been described earlier in a general way [1,2]: a diagram of it is shown in Fig. 3.

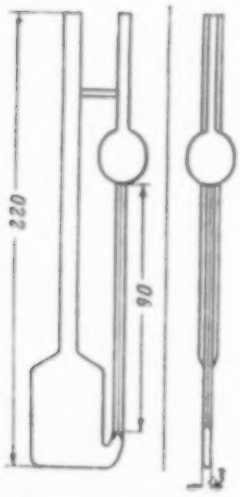

FIG. 2. Viscometer.

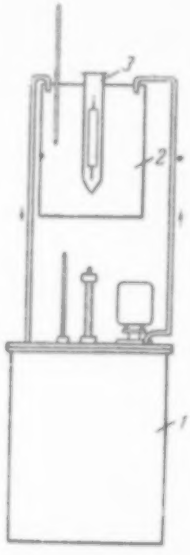

FIG. 3. Diagram of the apparatus (1) ultrathermostat, (2) glass container, (3) bulb PRK-2 in its cooling case.

The assembly was connected to the mains via a current stabiliser which provided stable working conditions for the PRK-2 lamp. The viscosity of the solution was measured in 10–30 min at the beginning of the experiment and somewhat less often at the end of the experiment. The data obtained were compared with the viscosity of the initial polyamide with the same molecular weight with the addition of a low, molecular compound. The duration of irradiation of the solution varied

from 50 to 150 hr. In some cases experiments were carried out at two different temperatures, namely at 20° and 50°C.

Measurement of the absorption spectra of the polyamide solutions was carried out in the laboratories of Academician I. V. Obreimov.

DISCUSSION OF RESULTS

It was established that the viscosity of polyamide solutions decreased sharply under the influence of irradiation and this depended on the duration of irradiation and the molecular weight of the initial polyamide: the larger the latter, the stronger the relative lowering of viscosity of its ethanolic solution in the initial radiation period. This meant that the longer polyamide molecules were less stable to radiation than the shorter ones. After some time (the smaller, the less the molecular weight of the polyamide) some stabilisation occurred, corresponding to a constant value for the viscosity. This state evidently corresponded to the equilibrium rate of disintegration and relinking of the macromolecule chains. Then increase in viscosity begins which was explained by the supremacy of the rate of reunion of the chains over the rate of breakdown. At this period of radiation the viscosity increased at different rates depending on the molecular weight of the polyamide. Low molecular specimens (mol. wt. 5000) showed the greatest increase inviscosity. A somewhat smaller increase was observed with a sample of molecular weight 12500 and a very small increase for polyamide with molecualar weight 23000.

A gradual slowing down of the rate of increase of viscosity was observed for low molecular polyamide, which was in the end equal to the rates found for the other two polyamides. At 50 hr irradiation the specific viscosities of all the solutions were approximately equal and corresponded to the viscosity of the initial solution of polyamide with mol. wt. 5000; longer irradiation had almost no effect on the viscosity of the polyamide solutions. It was possible that this was explained by the formation during the experiment of polyamide particles approximately equal in form and dimensions, which were affected little by ultra-violet irradiation. It was also probable that the shape of the particles formed would be spherical. The absorption spectra of the irradiated solutions of polyamide of various molecular weights, which are practically coincident, served as experimental proof of this. The absorption spectra of these solutions before irradiation differed strongly one from another, because the absorption was the stronger the greater the molecular weight. The change in spectral properties of the polyamides is shown in Fig. 1.

The viscosity of polyamide solutions in a mixture of dichloroethane and ethanol was also changed by radiation, but the rate of polyamide destruction in this solvent was sharply reduced in comparison with ethanol. The character of the specific viscosity curves was also changed. In these the last region, in which the viscosity increases noticeably, which is characteristic of a 50–60 hr radiation duration, is absent (Fig. 4, 1, 4, 7, and Fig. 5)

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The different behaviour of polyamides in this solvent was explained by their individual peculiarities. It may also be that dichloroethane, which is a good chain transfer agent, impeded the reunion of polyamide radicals.

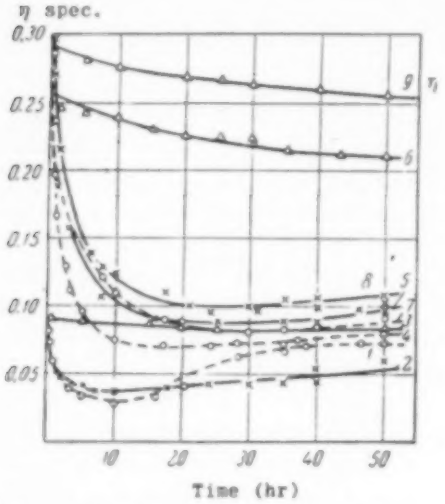

FIG. 4. The change in specific viscosity of the ethanol solutions of polyamide of various molecular weights under the influence of irradiation in the presence of 2-(*o*-oxyphenyl) benzoxazole (OFB), and without it. Polyamide of mol. wt. 5000; (1) without OFB; (2) 0·0005% OFB; (3) 0·4% OFB: polyamides of mol. wt. 12,500; (4) without OFB; (5) 0·0005% OFB; (6) 0·4% OFB; Polyamide of mol. wt. 23,000; (7) without OFB; (8) 0·0005% OFB; (9) 0·4% OFB.

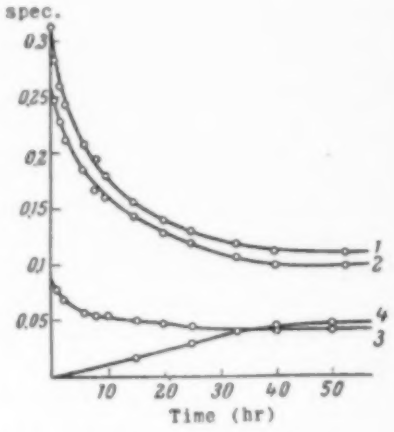

FIG. 5. The change in specific viscosity of solutions of different molecular weight in a mixture of ethanol and dichloroethane under the influence of irradiation: (1) mol. weight of 23,000; (2) mol. wt. of 12,500; (3) mol. wt. of 5000; (4) original solvent.

The influence of organic additives on the photochemical destruction process of polyamide solutions took a noticeable form. As is seen from Fig. 4, the addition of 0·4% of 2-*o*-hydroxyphenyl)-benzoxazole to an ethanolic polyamide solution noticeably lowered the rate of polymer destruction and decreased the chain rebuilding capacity in the radiation process (3,6,9). The experiment showed that a polyamide solution with this additive showed less reduction of specific viscosity after 150 hr irradiation, than after 5 hr without the additive. The polyamide solution with added 2-(*o*-hydroxyphenyl) benzoxazole gradually became coloured. A solution of low molecular polyamide became yellow coloured earlier than the others, and after 50 hr irradiation all the solutions became brown. The initial luminescence of the solutions disappeared more rapidly with the high molecular polyamides and less rapidly with the low molecular. It may be suggested that the

high molecular polyamides had a greater amount of disintegration and collision of the free radicals with particles of additive rapidly broke up the latter. After 50–70 hr irradiation a dark yellow deposit, which was so insignificantly small that it did not permit the elementary composition to be obtained, began to be precipitated from polyamide solutions with 0·4% of added 2-(*o*-hydroxyphenyl)-benzoxazole.

2-(*o*-hydroxyphenyl)-benzoxazole showed protective action at much lower concentrations, of the order of 0·0005% although the effect is less noticeable here (Fig. 4,2,5,8). The protective action is also shown in polyamide solutions in ethanol and dichloroethane mixture (Fig. 6).

The rate of polyamide destruction was noticeably increased if the experimental temperature was raised from 20° to 50°C. This was verified in polyamide solutions with 0·4% of 2-(*o*-hydroxylphenyl)-benzoxazole additive (Fig. 7).

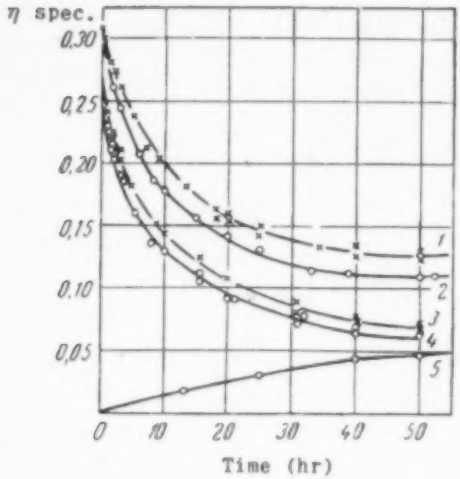

Fig. 6. The change in viscosity of solutions of polyamide in a mixture of dichloroethane and ethanol with the addition of 2-(*o*-oxyphenyl) benzoxazol (OFB) and without it. Mol. wt. of 23,000; (1) 0·0005% OFB; (2) without OFB; mol. wt. 17,000; (3) 0·0005% OFB; (4) without OFB; (5) solvent.

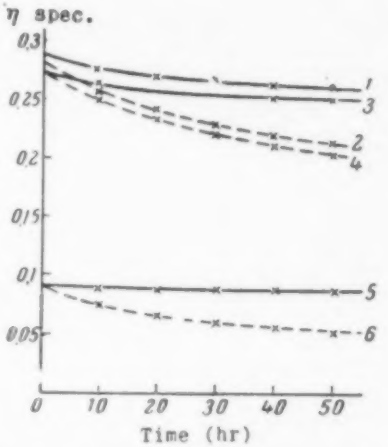

Fig. 7. The effect of temperature on the change in viscosity of ethanol solutions polyamides [with the addition of 0.4% 2-(*o*-oxyphenyl) benzoxazol]. Mol. wt. of 23,000; (1) 20°; (2) 50°: mol. wt. of 12,500; (3) 80°; (4) 50°: mol. wt. of 5000; (5) 20°; (6) 50°.

In these conditions solutions rapidly became coloured and the deposit precipitated in 30–40 hr irradiation instead of 50–70 hr.

The influence of another additive—dixanthylene—was tested in a polyamide solution in a mixture of ethanol and dichloroethane (dixanthylene is insoluble in alcohol). Two polyamide samples with molecular weights of 5000 and 23000 were investigated. From comparison of the graphs in Fig. 5 (1 and 2) and Fig. 8 (1 and 3)

it was seen that dixanthylene showed some retarding action on the process of photochemical breakdown of the polyamide. It may be suggested that the rapid disintegration of dixanthylene (observed earlier [1]) proceeded less fast in the solvent although after some hours of irradiation the intensity of luminescence of its solution decreased sharply. In the same way Fig. 8 showed the effect of 2-hydroxynaphthaldazine (2 and 4) which was investigated in the same way as dixanthylene. Comparison with Fig. 5 showed that 2-hydroxynaphthaldazine slightly delayed the destruction of the polyamide, but this effect gradually decreased. After 50–60 hr irradiation the rate of destruction of polyamide solutions with and without this additive became equal.

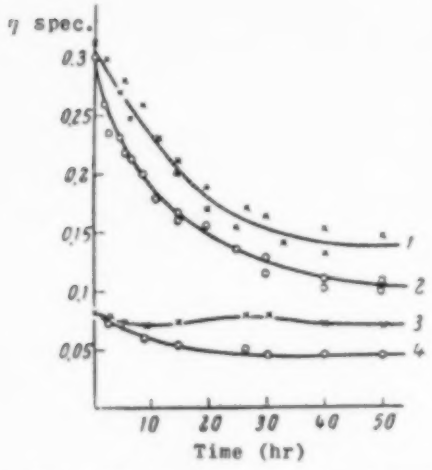

FIG. 8. The change in viscosity of solutions of polyamides in a mixture of dichloroethane and ethanol with the addition of dixanthylene (I) and oxynaphthaldazine (II) Mol. wt. 23,000; (1) 0·0005% I; (2) 0·0005% II: mol. wt. 5000; (3) 0·0005% I; (4) 0·0005% II.

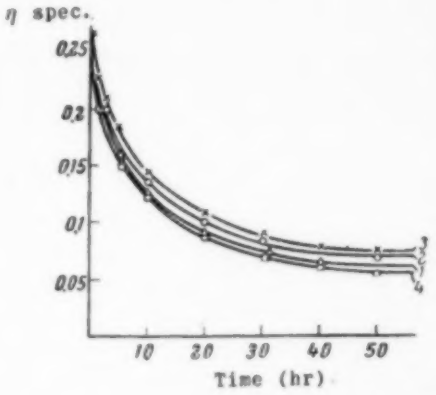

FIG. 9. The change in viscosity of solutions of polyamide (mol. wt. 17,000) in ethanol. (1) without addition; (2) 0·0005% β-methylumbellipherone; (3) 0·0005% salol; (4) 0·0005% N-monomethyltoluenesulphamide.

In Fig. 9 is shown the influence of three other low molecular weight compounds which were investigated for ethanolic solutions of polyamide with molecular weight 17000. The first two compounds—β-methylumbelliferone and salol (especially the former) showed a weak protective effect on the polyamide (1–3). This was in accord with earlier results on some protective affects of salol [1,2]. β-Methylumbelliferone was rapidly broken down by irradiation as the disappearance of luminescence from the polyamide solution with this additive showed [also 1]. N-methyltoluenesulphonamide in practice showed no effect on the destruction of polyamide. 2-hydroxybenzaldazine showed a sensitising effect on the disintegration of the polyamide, which is shown in Fig. 10.

This compound was not very stable to ultra-violet irradiation and it seemed that its decomposition gave rise to free radicals which accelerated the whole process of polyamide destruction.

To sum up the observations made, it can be said that the photochemical destruction of the polyamide anide G-669 in solution was retarded by some com-

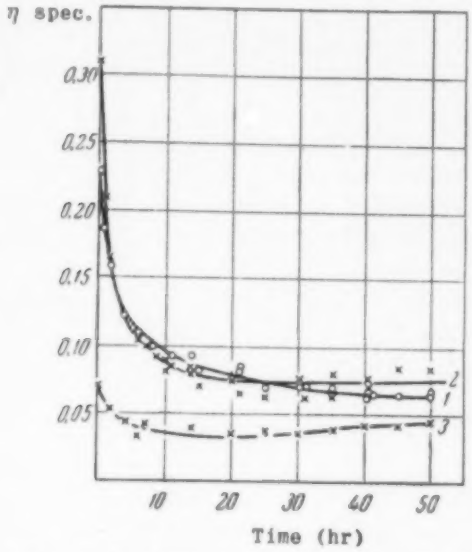

FIG. 10. The change in viscosity of ethanol solutions of polyamide in the presence of 0·0005% oxybenzaldazine (1) mol. wt. of 23,000; (2) mol. wt. of 12,500 (3) mol. wt. of 5000.

pounds, for example, 2-(*o*-hydroxyphenyl) benzoxazole, *β*-methylumbelliferone, salol, dixanthylene, and partly 2-hydroxynaphthaldazine. With the exclusion of the last, all the named compounds possess absorption spectra which overlap that of the polyamide in the 2800–2900 Å region and to a certain extent can act as filters of the ultra-violet radiation at these wavelengths. 2-(*o*-hydroxyphenyl)-benzoxazole showed the best protective effect of this group.

2-hydroxylbenzaldine and N-methyltoluene-sulphonamide were regarded as a second group. The first compound accelerated the process of photochemical disintegration of the polyamide, the second did not show a substantial effect, and while the first compound was luminescent the second was not. Thus, the present investigation showed that there was not a direct interdependence of the luminescent capacity, the corresponding spectral-absorption, and the action of the additive in decreasing the rate of change of viscosity of the polyamide solution.

On the basis of the present work and much earlier reports [1,2], it may be concluded that the ability to luminesce is not a deciding factor for a stabilising additive. The action of the latter is evidently based on the effect of screening the ul-

tra-violet radiation and, as has been shown earlier, inhibition of free radical formation by irradiation. The use of luminescent additives is desirable because luminophores are often more stable to ultra-violet radiation than non-luminescent compounds in general.

SUMMARY

(1) The photochemical destruction of polyamides was investigated.

(2) The dependence of the rate of destruction in the molecular weight was elucidated.

(3) The influence of different solvents on the character and rate of destruction of polyamide solutions was investigated.

(4) It was found that a direct relationship between the capacity for luminescence, the corresponding absorption spectra and the action of the tested low molecular additives did not exist.

(5) Of a number of additives used 2-(*o*-hydroxyphenyl) benzoxazole showed the best protective action.

Translated by M. J. NEWLANDS

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NUCLEAR MAGNETIC RESONANCE STUDIES—1 ON POLYMERS*

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(*Received* 27 *April* 1959)

INTRODUCTION

AFTER the discovery of electron paramagnetic resonance by Zaboucki in 1945, the analogous phenomenon was noted in relation to nuclei which possessed spin (Parsell and Bloch, 1946). Recently the nuclear magnetic resonance (NMR) method has been widely used for the investigation of the structure and properties of molecules in the liquid phase or in crystals[1]–[6]. On the one hand the NMR method permits the location of atomic positions in molecules and crystals, and the establishment of their structures; on the other hand it makes possible the investigation of relaxation, the kinetic properties of molecules and their separate parts, and the investigation of their mobility.

In recent years a series of papers has appeared devoted to the study of the structure and properties of polymers by the NMR method. A review of these papers up to 1958 is given in Slichter's article [7]. In the main the relaxation properties of polymers were reported in these, and in a broad way the influence of proton resonance on such factors as vulcanisation, filling, swelling and stretching of polymers was studied. In other words the influence of the indicated factors on the mobility of macromolecules in the solid was investigated. Some qualitative regularities were established which agreed with the generally accepted ideas of polymer physics.

In a series of papers the effect of the configuration and chemical structure of the polymer chain on its mobility in the glassy and visco-elastic states of the polymer was determined. (In some cases) The NMR method helped to ascertain the mobility of macromolecules and their separate parts at a temperature lower than T_c which succeeded in elucidating this for such groups of atoms as retain free rotation (e.g. CH_3 group in polymethylmethacrylate [8]). Crystalline polymers have been studied in great detail—polyamides, polyethylene, polytetrafluoroethylene

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[9], and very recently isotactic and atactic polypropylene [10]. The NMR method evidently permits the determination of the degree of crystallinity and the difference in mobility of a macromolecule in the crystalline and amorphous regions of the polymer.

However, all the work carried out up till now on the NMR investigation of polymers has an exploratory character. The principal possibilities of the method have been established but it has not lead to a systematic investigation of a series of suitable polymers for a detailed study of the influence of chemical structure on the mobility of macromolecules. The data obtained in the papers indicated has scarcely been subjected to any quantitative theoretical examination.

Undoubtedly the NMR method can give valuable information on the structure and properties of polymers both in the solid and in solution.* However to get really interesting and novel results a systematic investigation is necessary aimed at the solution of distinctly formulated problem. One of these problems which is particularly topical at the present time in the investigation of the effects of the stereochemical structure, the stereoregularity, of the polymer on its properties in the solid. The ability of the polymer to vitrify or crystallize depends directly on the stereochemical structure of the macromolecule. The mobility of the macromolecule in the vitreous and crystalline states, the transition point from one state into the other, and also the degree of crystallinity can be studied by the NMR method. At the same time calculations of the second moments of the resonance lines, leading to the method of configurational statsitics, can in principal, give interesting information on the structure of macromolecules.

Thus, as first problem we put before ourselves the study of stereoregular polymers. In the present communication the construction of our apparatus and the first results of the polymer investigations (samples of polymethylmethacrylate (PMMA) obtained under different conditions) are described.

APPARATUS FOR OBSERVING NMR SPECTRA

We constructed a radiospectrograph for the observation of NMR by the absorption method (Fig. 1).

The magnetic field of the spectrograph is established by an electromagnet with polar diameter of 154 mm and a distance between the poles of 25 mm (Fig. 2).

The yoke of the magnet is made of soft steel and the core of the coils of Armko iron. The lower core ends in a serical surface with a radius of 30 cm. On the latterph is located a ground polar tip which can be displaced on the sphere by means of three screws of small pitch. This regulation of the poles strictly parallel to one another is achieved without creating stress in the iron of the polar tips.

Apart from optical working of the flatness of the poles with a precision of up to 1μ over the whole surface, the uniformity of the field is improved by applying

* Polymer solutions have not yet been studied by this method.

a ring to the pole, which weakens local effects. The uniformity of the magnetic field is determined by the alternation time of the transfer processes (wiggles) which are observed if the NMR signals pass sufficiently fast.

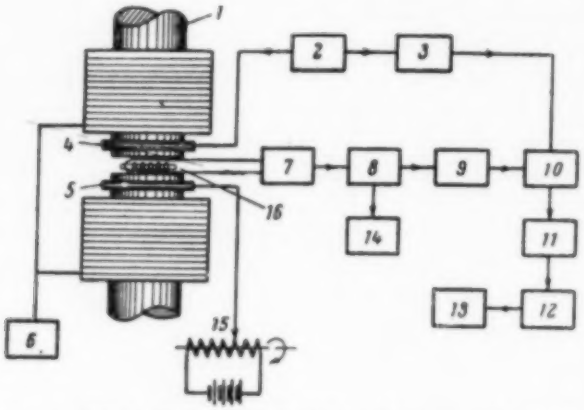

FIG. 1. Block diagram of N.M.R. radiospectrograph. (1) electromagnet; (2) audiogenerator, ZG-10, (3) phase-rotator; (4) modulating coil, (5) coil for altering magnetic field. (6) power for magnet. (7) regenerative generator (20mc/s); (8) Amplifier for lower pars (9) narrow-band amplifier (10) phase-sensitive detector (11) Constant current amplifier (12) Cathodic repeater (13) Recorder EPP-09 (14) Oscilloscope EO-7 (15) Slide-wire (16) Generator coil with sample.

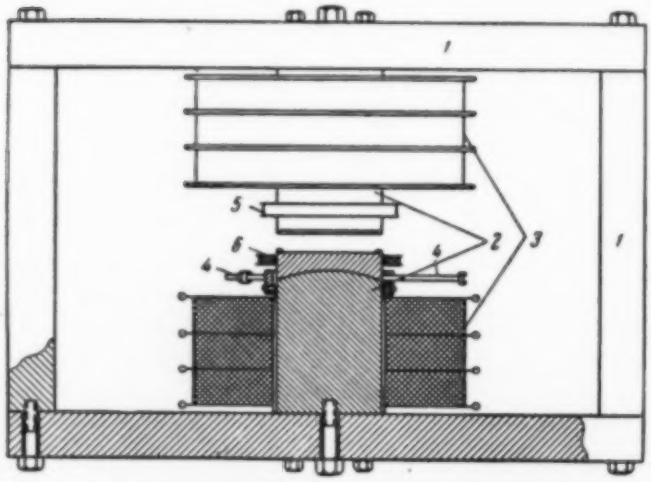

FIG. 2. Electromagnet. (1) Yoke; (2) core coils; (3) windings; (4) screws regulating "parallelness" of poles; (5) modulating coil; (6) coil for altering magnetic field

In Fig. 3 a and b, are present the NMR signals for protons in water, from which the numerical value of the inhomogeneity of the field, ΔH, in the volume of the sample was determined.

$$\Delta H = \frac{1}{|\gamma| T_2^*},$$

where γ = gyromagnetic ratio and T^* = alternation time of the wiggles in seconds. For our magnet the value of ΔH was not worse than 0·03 G. for a field strength

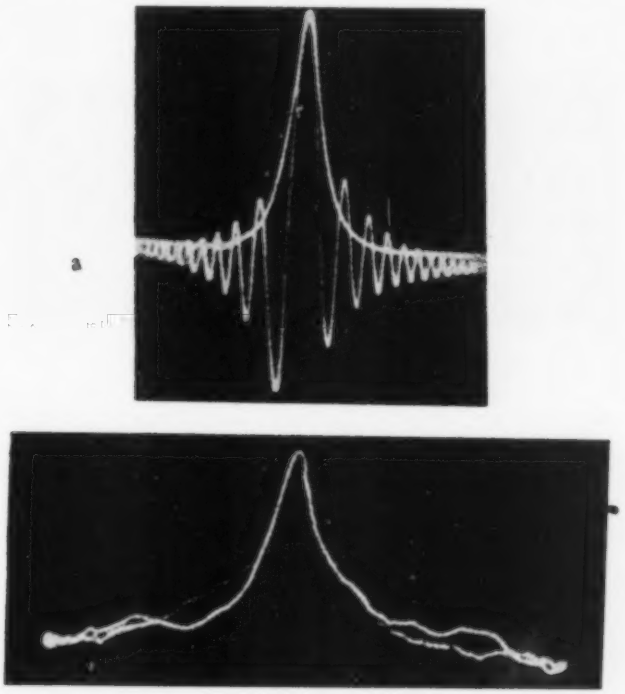

FIG. 3. N.M.R. Signal of protons: (a) in water, H_a=0·8 c/s. (b) in polyethylene at 20°, H_a=18·5 c/s.

of 5000 G. If necessary the stability of the field in our apparatus may be materially improved. The windings of the electromagnet are constructed from 3600 spirals of copper wire PBD of diameter 2·44 mm, divided into six sections with copper disc, to the outside edge of which are soldered tubes for circulating cooling water for the magnet. The magnet is supplied from a battery of acid accumulators with a tension of 32V and a capacity of 900 A hr. The maximum power of the magnetic field was 13000 G. Experiments were carried out with a field of 5000 G; with this field the drift during the warming-up period was not greater than 3 G per hour. The effect of drift on the measured results was eliminated by a forward and backward tracing of the spectrum.

An audiogenerator ZG-10 is used for the modulation of the magnetic field which is necessary for observing the spectrum. A frequency of 31·8 c/s is fed into a modulation coil with a resistance of 700Ω which covers the upper coil. The doubling amplitude of modulation H_s has a maximum value of 18·5 G and may be decreased to $^1/_{450}$ of this size without change of strength of the audiogenerator which is important for the normal working of the phase detector.

For investigation of the signals of NMR absorption the method of generator of weak oscillation is used. A high-frequency (20 Mc/s) regenerative generator, in the contour coil of which is placed the substance being investigated, is assembled by Hopkins' scheme [11] and mounted as a separate block.

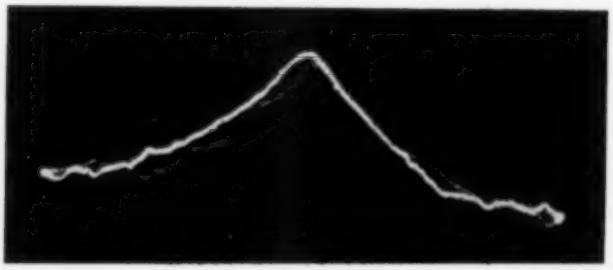

FIG. 4. N.M.R. Signal of the F^{19} nucleus in polytetrafluorethylene at 20°, $H_s = 18{\cdot}5$ c/s.

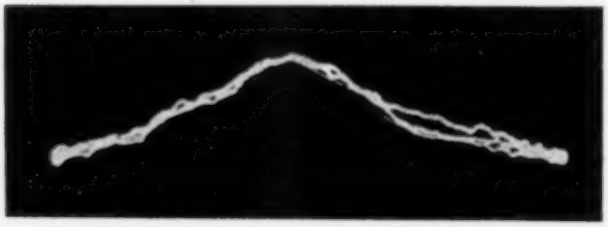

FIG. 5. N.M.R. Signal of protons in polymethylmethacrylate $H_s^1 = 18{\cdot}5$ c/s.

To achieve maximum sensitivity the level of generation should be minimal in order to regulate the positive inverse relation. After detection in a valve, the nuclear absorption signal goes through a double-cascade low frequency amplifier to an oscillograph EO-7 (Fig. 3, 4, 5, 6). The resonance line observed on the oscillograph screen is broad and weak, and equal to the noise level and is not suitable for obtaining quantitative results. Therefore a phase-sensitive detector method was used which noticeably increased the signal to noise ratio. With this method the modulating amplitude should be increased to a value not greater than 1/6th of the width of the resonance line, and one should ensure the slow passage of either the generator frequency or the field strength across the resonance region. In our apparatus the magnetic field is changed. To do this a field which rises or falls linearly with time and which is obtained by using a special slide-wire is fed

into a coil surrounding the lower pole tip. To decrease the non-linearity of the slide-wire a bridge is included in the scheme. The rate of field change in this case varies with the changed size of the current feeding the bridge scheme with the slide-wire. The nuclear absorption signal is put into a narrow-band amplifier,

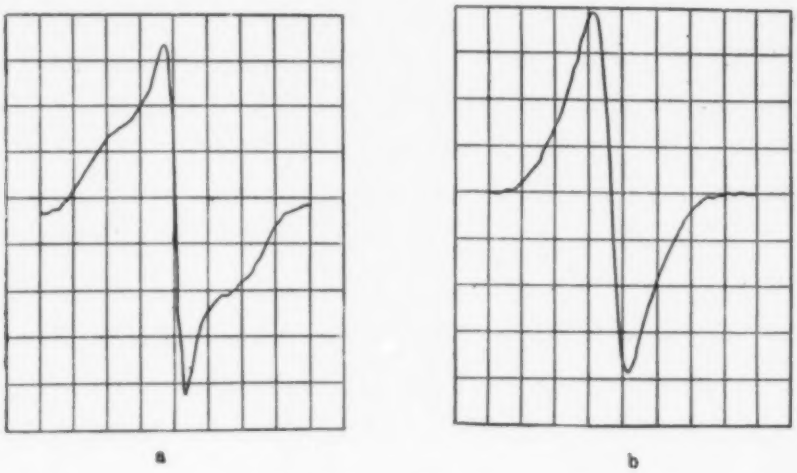

FIG. 6. Derivatives of the N.M.R. Signal (a) for polytetrafluoroethylene; (b) for polymethylmethacrylate.

with twin T-type filters in line with the inverse relation. This amplifier has a selectivity of 0·03 at frequency of 31·8 c/s. Then the amplified signal is put into a phase-detector which is connected according to Shooster's scheme [12]. From the exit of the phase detector is obtained the derivative of the signal of the absorption at the field strength. This is amplified with a two-cycle amplifier at constant voltage, and put into a recording potentiometer EPP-09 (Fig. 6) via a cathodic repeater.

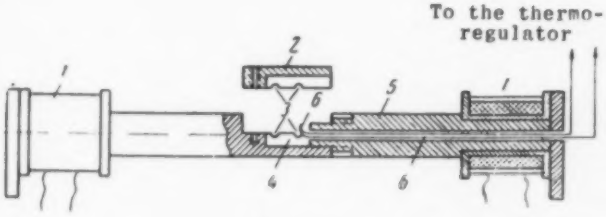

FIG. 7.

In order that the shape resonance line should not be distorted by the RC-line of the phase detector, the time of sweep should be noticeably increased with the RC-line time constant, which determines the permitted period of the system.

For investigation of polymers at different temperatures a heater was constructed (Fig. 7) which embodied a copper core, on both ends of which heating coils were wound. In the central part of the core, which is introduced into the magnetic field, is a cavity in which the tube of sample is placed. The cavity is tightly sealed with a lid which provides good heating conditions and also screens the coils. A hot gas is passed through the tube in contact with the solvent. The whole of the structure is wrapped with asbestos string on the outside to insulate it thermally.

PRELIMINARY RESULTS OF AN INVESTIGATION OF PMMA

We investigated a series of samples of PMMA which were made in Korotkov's laboratories, and also common technical PMMA (plexiglass). The samples had the properties shown in the Table.

TABLE 1. PROPERTIES OF THE POLYMETHYLMETHACRYLATE SAMPLES STUDIED

Sample No.	Method of preparation	Stereochemical structure	Density	M. wt.	T_c(°C)	T'_c(°C)
1	Radical (technical plexiglass)	Atactic	1·18	$\sim 10^6$	100	90
2	The same	,,	1·20	$\sim 10^6$	120	135
3	Catalytic	Isotactic	1·22	$1{\cdot}2 \times 10^5$	74	60
4	The same	,,	1·22	3×10^5	46	54
5	The same	,,	1·22	$1{\cdot}3 \times 10^5$	60	50

All samples were amorphous as demonstrated by X-rays. The second moments $\overline{\Delta H^2}$ for all samples at room temperature were calculated from the recorded derivative curves of NMR absorption as the magnetic field changed. The values of $\overline{\Delta H^2}$ obtained were shown to lie between the limits 6·0 to 9·5 c/s², which concurred with the results obtained by Odajina, Sohma and Koike [8], who obtained for radical PMMA at 20°C a value for $\overline{\Delta H^2}$ equal to 8·5 c/s². These authors calculated theoretically the second moment for the PMMA monomer, obtaining a value of $\overline{\Delta H^2}$ equal to 7·8 c/s² as a result.

In addition we studied the dependence of proton resonance line width on temperature. The NMR lines narrowed with increasing temperature for all samples which corresponds to increasing mobility of the macromolecules. The character of corresponding curves is substantially different for the five samples examined. We see that the samples obtained by radical means are characterised by a lower molecular mobility, than those made catalytically. This is in accordance with the much higher softening temperature T_c and effective temperature of resonance line narrowing T'c, established from the intersection of tangents (Fig. 8), of "radical" samples of PMMA.

The character of line narrowing is also very significant. Isotactic samples (especially sample 4) displayed a very sharp narrowing. The second moment of sample 4 decreased from 7·8 to 1·9 c/s^2 on changing the temperature from 50 to

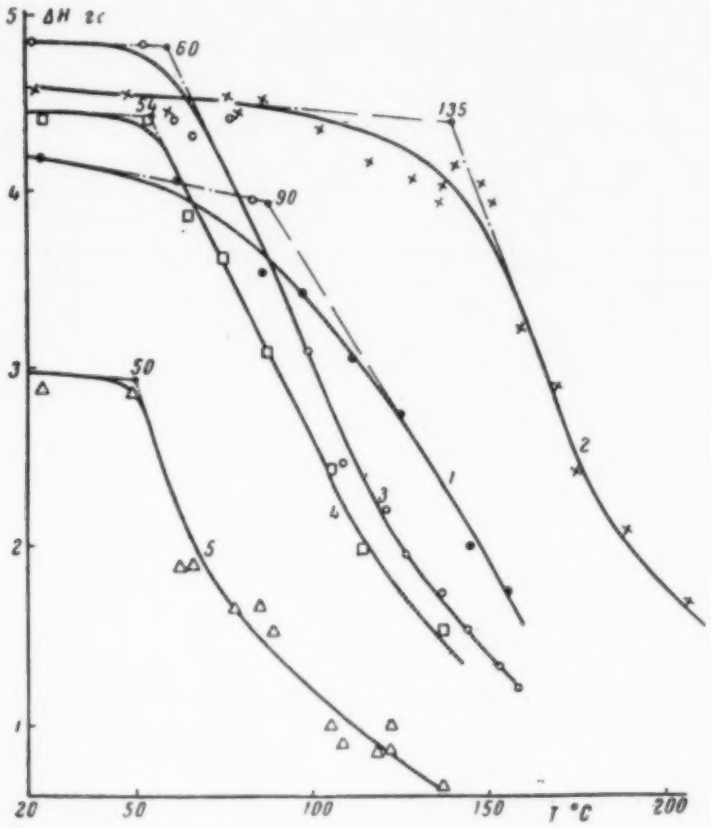

FIG. 8. Dependence on temperature of the PMMA resonance line width. (1) sample 1; (2) sample 2; (3) sample 3; (4) sample 4; (5) sample 5.

120°C. On the other hand, the lines of the radical samples 1 and 2 narrowed gradually.

The results obtained up till now are insufficient for a detailed interpretation of the molecular mobility of atactic and isotactic PMMA. The great mobility of the chain of isotactic samples of PMMA which was detected by us agrees with the greatly reduced value of the vitrification temperature. These facts are to some extent unexpected: it would be natural to suppose that increased stereoregularity of the chain which leads to closer packing in the solid, should decrease, not increase, the mobility. It is evident that the connection between the kinetic and

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structual characteristics of a polymer are more complicated. To interpret the data obtained it is necessary to establish by what the observed linė narrowing is determined—by the mobility of the chain intact or as several pieces. This requires long systematic experimental investigations and theoretical calculations.

We thank K. V. Vladimirski and F. I. Skripov for advice on the experimental methods of NMR.

SUMMARY

(1) A radiospectrograph was constructed for observing NMR by the absorption method. The uniformity of the magnetic field reached $6 \cdot 10^{-6}$. The phase-sensitive detector method was used as a method of increased sensitivity. The apparatus was intended for the investigation of polymer relaxation properties.

(2) The dependence of the half width of the proton magnetic resonance lines on the temperature was investigated for five samples of polymethylmethacrylate which were obtained by radical and catalytic polymerisation. The calculated second moments of these sample at room temperature agreed with those in the literature.

(3) The samples which were obtained by catalytic polymerisation and contained isotactic chains were characterised by a greater molecular mobility.

Translated by M. J. NEWLANDS

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ON THE ENTROPY ELASTICITY OF A CONTINUOUS INCOMPRESSIBLE MEDIUM CONTAINING RIGID ANISOTROPIC PARTICLES

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(*Received* 28 *April* 1959)

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THE theory of the elastic properties of amorphous polymers, regarded as a condensed medium, may proceed from the description of the structure of these substances [1]. In connection with this it is necessary to investigate the behaviour of rigid anisotropic particles in a continuous deformable medium and its absorption. Such particles do not stretch in deformable media, but they change their orientation. In unstretched samples they are orientated randomly and on stretching the orientation distribution function is changed. The model described was first examined by Kuhn [2] but it was restricted to cases of maximal anisotropy.

Kuhn constructed a theory of the elastic properties of a polymeric medium containing strongly stretched crystallites. He suggested that this could be used for partially crystalline polymers.

Kuhn and Grun [3] considered that the orientation of the crystallites was the cause of the photoelastic effect in polymers. However the results obtained were contrary to experiment. The observed double refraction of an amorphous polymer was noticeably lower than would be expected on the basis of the crystallite orientation concept. On the other hand, an examination of the Gaussian distribution of the polymer chains gave a reasonable explanation of the observed facts [3]. Nevertheless the results obtained by Kuhn are useful for solving our problem.

We shall introduce a short account of Kuhn's theory [1–5]. The crystallite is characterized by the orientation of a single vector of its own length which we shall call $\vec{s}$. Kuhn examined the limiting anisotropic crystallites which had no thickness. The probability that the angle subtended by the vector $\vec{s}_i$ of the i^{th} crystallite and some axis z lies between ϑ_i, $\vartheta_i + d\vartheta_i$, is equal to

$$w_i = \frac{1}{2} \sin \vartheta_i d\vartheta_i . \tag{1}$$

* Vysokomol. soedin. **1**: No. 7, 1063–1069, 1959.

The probability that $v_1, v_2, \ldots\ldots, v_n$ crystallites are respectively in the intervals $d\vartheta_1, d\vartheta_2, \ldots\ldots d\vartheta_n$, is equal to

$$W=\prod_{i=1}^{n}(w_i)^{v_i}\frac{G!}{\prod_i v_i!}, \tag{2}$$

where

$$G=\sum_i v_i \tag{3}$$

—the total number of crystallites. From the condition of maximum entropy

$$S=k\ln W \tag{4}$$

we get

$$v_{i_0}=\frac{1}{2}G\sin\vartheta_i d\vartheta_i \tag{5}$$

and the entropy of this most probable state

$$S_0=0.$$

Thus in a non-deformable medium the distribution (5) according to the angle ϑ is isotropic. The distribution according to the angle φ does not change with stretching along the z axis.

Let us pass now to a medium which is stretched along the z axis.

The coordinates of the ends of the vectors $\overrightarrow{s_1}$ in the unstretched medium are:

$$x_i=s_i\sin\vartheta_i\cos\varphi_i,$$
$$y_i=s_i\sin\vartheta_i\sin\varphi_i,$$
$$z_i=s_i\cos\vartheta_i$$

$$\operatorname{tg}\vartheta_i=\frac{\sqrt{x_i^2+y_i^2}}{z_i}.$$

On stretching an incompressible polymer along the z axis λ times, the coordinates x_i, y_i, z_i change into

$$x_i'=\frac{1}{\sqrt{\lambda}}x_i,\quad y_i'=\frac{1}{\sqrt{\lambda}}y_i,\quad z_i'=\lambda z_i \tag{7}$$

and the angle ϑ_i into angle

$$\vartheta_i'=\operatorname{arc\,tg}(\lambda^{-3/2}\operatorname{tg}\vartheta_i). \tag{8}$$

Correspondingly the distribution (5) changes into

$$v_i=\frac{G}{2}\frac{\lambda^{3/2}\sin\vartheta_i d\vartheta_i}{[\lambda^{-3/2}\cos^2\vartheta_i+\lambda^{3/2}\sin^2\vartheta_i]^{3/2}}.$$

The difference of entropy in the stretched and unstretched state is:

$$(S-S_0)_{\text{orient}}=S_{\text{orient}}=G\ln G+$$

$$+k\sum_i\left\{\frac{G}{2}\frac{\lambda^{3/2}\sin\vartheta_i d\vartheta_i}{[\lambda^{-3/2}\cos^2\vartheta_i+\lambda^{3/2}\sin^2\vartheta_i]^{3/2}}\ln\frac{\sin\vartheta_i d\vartheta_i}{2}-\right.$$

$$-\frac{G}{2}\int\frac{\lambda^{3/2}\sin\vartheta_i d\vartheta_i}{[\lambda^{-3/2}\cos^2\vartheta_i+\lambda^{3/2}\sin^2\vartheta_i]^{3/2}}\left[\ln G+\ln\frac{\sin\vartheta_i d\vartheta_i}{2}+\right.$$

$$\left.+\ln\frac{\lambda^{3/2}}{[\lambda^{-3/2}\cos^2\vartheta_i+\lambda^{3/2}\sin^2\vartheta_i]^{3/2}}\right]\Bigg| \tag{10}$$

and, changing from summation to integration, we get

$$S_{op}=3\,kG\left[1-\ln\lambda-\frac{1}{(\lambda^3-1)^{1/2}}\operatorname{arc\,tg}(\lambda^3-1)^{1/2}\right] \tag{11}$$

and the expression for the condition of tension is

$$\sigma=-T\frac{\partial S_{op}}{\partial\lambda}=\frac{3G\,kT}{2\lambda(\lambda^3-1)}\left\{2\lambda^3+1-3\lambda^3\frac{\operatorname{arc\,tg}(\lambda^3-1)^{1/2}}{(\lambda^3-1)^{1/2}}\right\}. \tag{12}$$

The modulus of elasticity is

$$\varepsilon=\left(\frac{\partial\sigma}{\partial\lambda}\right)_{\lambda=1}=\frac{9}{5}GkT. \tag{13}$$

However, Kuhn's calculations did not take into account the form of the crystals which took the place of the vector $\vec{s}$. Evidently, the strength of σ should depend on the anisotropy of form of the orientated particles, becoming zero for isotropic particles. Let us carry out the corresponding calculation.

Let us characterize the rigid particle not by one but by three mutually perpendicular vectors of length $\vec{a}$, $\vec{b}$, and $\vec{b}$. In other words we shall consider a particle to possess axial symmetry. In this case the orientation of the particles may be as in the previous problem with one angle ϑ between the z axis of the coordinate system, which is fixed in the sample and isolated from the a axis of the particle (Fig. 1). The distribution of the angles is found by starting from the following considerations. It is possible that on a rigid anisotropic particle in a deformable continuous medium, there acts a resisting force which is opposite in direction to the rate of motion relative to the medium of a point on the particle surface, and proportional to its size.

$$\vec{f}_i=-\overrightarrow{k^i r_i},$$

where r_i is the relative speed of the i^{th} point on the particle.

We will limit the examination to the movement of the ends of the vectors $\vec{a}$ and $\vec{b}$ lying in the plane xz. In the presence of such a force, the equation of motion of the system has the form

$$\frac{d}{dt}\left(\frac{\partial T}{\partial\dot{q}_i}\right)-\frac{\partial T}{\partial q_i}=-\frac{\partial U}{\partial q_i}-\frac{\partial R}{\partial\dot{q}_i} \tag{14}$$

where q_i—generalised coordinate, T—kinetic, and U—potential energy of the system, and R—Raleigh's dissipation function which is a measure of the dispersion of mechanical energy in unit time, caused by a resisting force

$$R=\frac{1}{2}\sum_i k_i\left(\frac{\dot{r}_i}{r_i}\right)^2=\frac{1}{2}\sum_i k_i r_i^2. \tag{15}$$

Let us suppose that the particle is moved without inertia and does not change its potential energy on moving. Then the equation of motion reduces to

$$\frac{\partial R}{\partial \dot{q}_i}=0.$$

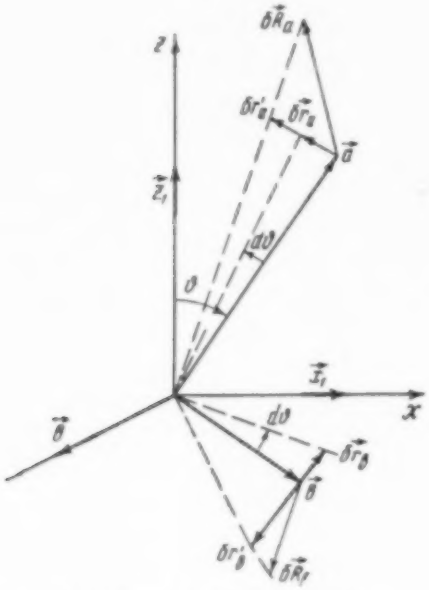

FIG. 1. Calculation of the distribution function.

In our case $q=\vartheta$, the velocity v_i has sense relative to the velocity of the ends of the vectors $\vec{a}$ and $\vec{b}$ in the medium, i.e.

$$v_i=v_{i\,\text{frequency}}-v_{i\,\text{cp}},$$

where

$$v_{i\,\text{frequency}}=r_i\dot{\vartheta}.$$

We have, with an increase in time of δt,

$$\frac{\partial R}{\partial \vartheta}\delta t=k\sum_i r_i\left(v_{i\,\text{frequency}}-v_{i\,\text{cp}}\right)\delta t=k\sum_i r_i\left(\delta r'_i-\delta r_i\right)=0, \tag{17}$$

where $v_{i\,\text{cp}\,\vartheta}$—the projection of the rate of displacement of the medium on the firection of the particle velocity, $\delta r'_i$—the projection of the displacement of a point in the medium $\overrightarrow{\delta R}$ before deformation, coinciding with a point r_i (see Fig. 1). In our case we have

$$a\left(\delta r'_a-\delta r_a\right)+b\left(\delta r'_b-\delta r_b\right)=0. \tag{18}$$

where $$\delta r'_a = \frac{\delta \vec{R}_a \, \delta \vec{r}_a}{\delta r_a}, \quad \delta r'_b = \frac{\delta \vec{R}_b \, \delta \vec{r}_b}{\delta r_b}.$$

In a medium, which is deformed in conformity with condition (7), we have with deformations λ and $\lambda' = \lambda + \delta\lambda$

$$\begin{aligned} z_a &= \lambda z_a(0), \quad x_a = \frac{1}{\lambda^{1/2}} x_a(0), \\ z'_a &= \lambda z_a(0), \quad x'_a = \frac{1}{\lambda^{1/2}} x_a(0), \end{aligned} \tag{19}$$

where $x_a(0)$, $z_a(0)$ are coordinates of the point $\vec{a}$ in the undeformed sample.

Consequently,

$$\delta \vec{R}_a = z_1 (\vec{z'_a} - z_a) + \vec{x}_1 (x'_a - x_a), \tag{20}$$

where $\vec{z}_1$, $\vec{x}_1$ are unit vectors. Substituting (19) into (20) we get

$$\delta \vec{R}_a = \vec{z}_1 z_a(0) (\lambda' - \lambda) + \vec{x}_1 x_a(0) \left(\frac{1}{\lambda'^{1/2}} - \frac{1}{\lambda^{1/2}} \right) \tag{21}$$

or because $$z_a(0) = \frac{1}{\lambda} z_a, \; x_a(0) = \lambda^{1/2} x_a$$

$$\delta \vec{R}_a = \vec{z}_1 z_a \frac{\delta\lambda}{\lambda} - \vec{x}_1 x_a \frac{\delta\lambda}{\lambda^{3/2}} \lambda^{1/2} = \vec{z}_1 a \cos\vartheta \frac{\delta\lambda}{\lambda} - \vec{x}_1 a \sin\vartheta \frac{\delta\lambda}{2\lambda}. \tag{22}$$

At the same time

$$\delta \vec{r}_a = -\vec{z}_1 a \sin\vartheta \delta\vartheta + \vec{x}_1 a \cos\vartheta \delta\vartheta, \quad \delta r_a = a \delta\vartheta \tag{23}$$

and $$\delta r'_a - \delta r_a = \frac{\delta \vec{R}_a \, \delta \vec{r}_a - (\delta r_a)^2}{\delta r_a} = -\frac{3}{4} a \sin 2\vartheta \frac{\delta\lambda}{\lambda} - a \delta\vartheta. \tag{24}$$

In a similar way we find

$$\delta r'_b - \delta r_b = \frac{3}{4} b \sin 2\vartheta \frac{\delta\lambda}{\lambda} - b \delta\vartheta. \tag{25}$$

Equation (18) takes the form

$$\frac{3}{4} (b^2 - a^2) \sin 2\vartheta \frac{\delta\lambda}{\lambda} - (b^2 + a^2) \delta\vartheta = 0. \tag{26}$$

Integrating (26) within the limits from 1 to λ and, correspondingly from ϑ to ϑ^1, we get

$$\operatorname{tg}\vartheta' = \lambda^{\frac{3}{2}\frac{b^2-a^2}{b^2+a^2}} \operatorname{tg}\vartheta. \tag{27}$$

With $b=a$ and $\vartheta^1=\vartheta$ the distribution of angles does not change. With $b=0$ we get Kuhn's equation

$$\operatorname{tg}\vartheta' = \lambda^{-3/4} \operatorname{tg}\vartheta.$$

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Evidently we may change from the case examined by Kuhn into our case by changing λ in the entropy expression (11) into

$$\lambda_{\text{eff}} = \lambda^{\frac{a^3-b^3}{a^3+b^3}} = \lambda^{\frac{p^3-1}{p^3+1}}, \tag{28}$$

where $p=a/b$

Correspondingly, the force expression takes the form

$$\sigma = -T\frac{\partial S_{\text{op}}}{\partial \lambda} = -T\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\frac{\partial \lambda_{\text{eff}}}{\partial \lambda} = -T\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\frac{\beta}{3}\lambda^{\beta/3-1} \tag{29}$$

or

$$\sigma = \frac{\beta GkT}{2\lambda(\lambda^{\beta}-1)}\left\{2\lambda^{\beta} = +1-3\lambda^{\beta}\frac{\operatorname{arc\,tg}(\lambda^{\beta}-1)^{1/2}}{(\lambda^{\beta}-1)^{1/2}}\right\}, \tag{30}$$

where

$$\beta = 3\frac{p^2-1}{p^2+1} \text{ with } \lambda = 1{,}6 = 0.$$

The modulus of elasticity, according to (13) and (29), is

$$\varepsilon = \left(\frac{\partial \sigma}{\partial \lambda}\right)_{\lambda=1} = -\frac{\beta}{3}T\left\{\frac{\partial}{\partial \lambda_{\text{eff}}}\left(\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\right)\frac{\partial \lambda_{\text{eff}}}{\partial \lambda}\lambda^{\beta/3-1}\right\}_{\lambda=1} -$$

$$-\frac{\beta}{3}\left(\frac{\beta}{3}-1\right)T\left\{\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\lambda^{\beta/3-2}\right\}_{\lambda=1} =$$

$$= -\frac{\beta^2}{9}T\left\{\frac{\partial}{\partial \lambda_{\text{eff}}}\left(\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\right)\lambda^{2\beta/3-2}\right\}_{\lambda=1} - \frac{\beta}{3}\left(\frac{\beta}{3}-1\right)T\left\{\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\lambda^{\beta/3-2}\right\}_{\lambda=1} \tag{31}$$

and, because with $\lambda=1$, $\lambda_{\text{eff}}=1$

$$\left(\frac{\partial S(\lambda_{\text{eff}})}{\partial \lambda_{\text{eff}}}\right)_{\lambda_{\text{eff}}=1} = \left(\frac{\partial S(\lambda)}{\partial \lambda}\right)_{\lambda=1} = 0$$

and

$$-T\left\{\frac{\partial}{\partial \lambda_{\text{eff}}}\left(\frac{\partial S_{\text{op}}}{\partial \lambda_{\text{eff}}}\right)\right\}_{\lambda_{\text{eff}}=\lambda=1} = \frac{9}{5}GkT$$

(Cf, $T(13)$), we get

$$\varepsilon = \frac{1}{5}GkT\beta^2 = \frac{9}{5}GkT\left(\frac{p^2-1}{p^2+1}\right)^2. \tag{32}$$

Let us examine two extreme cases: $b=0$, $p=\infty$ ("needles") and $a=0$, $p=0$ (circular "plates"). The first case concurs with Kuhn's investigations, but in the second case

$$\sigma = \frac{3GkT}{2\lambda(\lambda^3-1)}\left\{2+\lambda^3-3\frac{\operatorname{Arth}\left(\frac{\lambda^3-1}{\lambda^3}\right)^{1/2}}{\left(\frac{\lambda^3-1}{\lambda^3}\right)^{1/2}}\right\}. \tag{33}$$

It will be recalled that

$$\operatorname{Arth} x = \frac{1}{2}\ln\frac{1+x}{1-x} \qquad (x<1). \tag{34}$$

The module of elasticity are equal in the two cases.

In Fig. 2 is presented the dependence of 6 (λ) (on the tension) for "needles" and "plates", described by formulae (12) and (33). With small λ the curves coincide, with $\lambda \gg 1$ the function (12) tends to 0 as $3\lambda^{-1}$ but the function (33) tends to zero as $\frac{3}{2}\lambda^{-1}$.

In the case of isotropic particles $\vec{a}=\vec{b}$, $p=1$, $\beta=0$, the entropy of orientation force changes to zero. The curve of 6 (λ) for values of $p > 1$ is situated in the space between the abscissa and curve 1 (Fig. 2), and for values of $p < 1$ between the abscissa and curve 2.

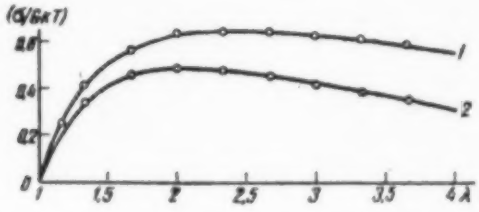

Fig. 2. Dependence of tension on deformation.

On the basis of the calculations carried out the assumption is proposed that the force which acts on a rigid particle in a continuously deformable medium, is proportional to the rate of movement i.e. it has the character of a frictional force. The result obtained in this way does not depend on the coefficient of friction K. Such an assumption is analogous to that used in the theory of the orientation of particles in a flowing medium [7,8]. Considering that rigid particles contain very many atoms, we may not consider the role of Brownian movement in establishing equilibrium.

The calculation is not exact, because the resisting force acting on all points of the surface of the particle changes with the force acting on the axis of the particle. However it may be thought that an exact calculation, meeting with notable mathematical difficulties and demanding a knowledge of the shape of the particles, would not lead to results which differed materially from those described.

In the present calculation the influence of the volume of the particles examined on the elastic properties of the system is not considered in any way. It is true that such effects do tell on the mechanical properties of filled polymers. However the theory expounded should be applied to the examination of the properties of polymers containing crystallites or large anisotropic particles of filler, if these properties depend substantially on the orientation of the particles. We think that the theory correctly explains the experimental data relating to the photoelastic effect in systems containing rigid particles with optical

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anisotropy which noticeably increased the effective anisotropy of the surrounding medium. In this case the phenomenon should not depend strongly on the volume of the particles. We propose to return to this question later.

The application of the theory to the examination of properties of amorphous polymers is discussed in the previous paper [1].

SUMMARY

(1) A calculation has been carried out, concerning the dependence of the entropy on deformation for an elastic, incompressible medium containing rigid anisotropic particles.

(2) The dependence of the elastic entropy force on the form of the particles has been investigated. In the limiting case of elongated particles ("needles") the theory led to a result obtained earlier by Kuhn. For isotropic particles the elastic force is reduced to zero. For the other limiting case ("plates") the dependence of the force on the deformation obtained was in general similar in form to the dependence for "needles". The initial moduli of elasticity of the two limiting cases were equal.

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INCREASING THE THERMAL STABILITY OF POLYMERS BY CYCLIZATION IN MACROMOLECULAR CHAINS DURING THEIR PARTIAL DECOMPOSITION*

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(*Received* 5 *May* 1959)

IN the thermal decomposition of polar polymers such as polymethyl methacrylamide and polymethacrylic acid volatile products (methylamine and water) are evolved and cyclic structures formed in the primary valence chains. This results in the thermal stability of the polymers being considerably increased. Figure 1 and 2 show kinetic curves for thermal decomposition of polymethyl methacrylamide and polymethacrylic acid *in vacuo*. In both cases two stages of decomposition are observed.

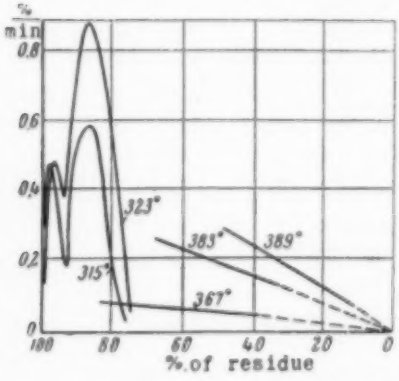


Fig. 1. Kinetic curves of the decomposition of polymethyl methacrylamide *in vacuo*. Curves at 367, 383 and 389° refer to a polymer pre-cyclized *in vacuo* at 320°.

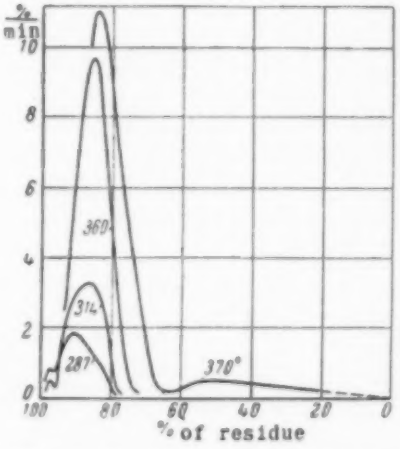
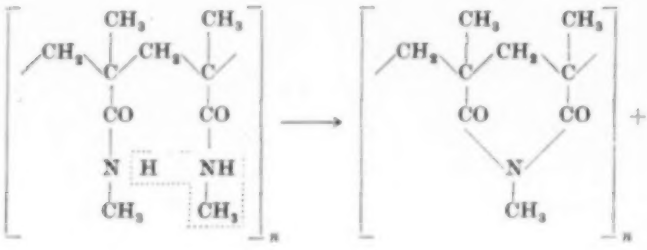


Fig. 2. Kinetic curves of the decomposition of polymethacrylic acid *in vacuo*.

After some partial decomposition of the polymers their rate of decay becomes insignificant and further decay takes place only at considerably higher temperatures.

* Vysokomol. soedin. 1: No. 7, 1070–1073, 1959.

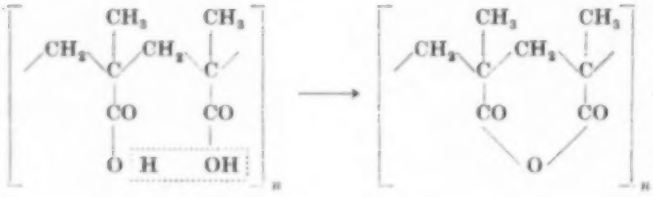
In the case of polymethyl methacrylamide, deamination of the polymer takes place at first with the evolution of volatile methylamine and the formation of a stable six-membered ring. In this way a polymer with polar side groups becomes a polymer with a cyclized chain, which explains the increase in the thermal stability of the partially disintegrated polymer as compared to the initial compound. The polymer remains linear and soluble. It is interesting to note that if the initial polymethyl methacrylamide is soluble in water, it loses this ability after cyclization, but becomes soluble in benzene and chloroform. Crouwels and Smets have already demonstrated the possibility of nitrogen-containing rings forming in the polymer chain of methacrylamide [1]. The deamination reaction of polymethyl methacrylamide can be represented by the following equation:



(1)

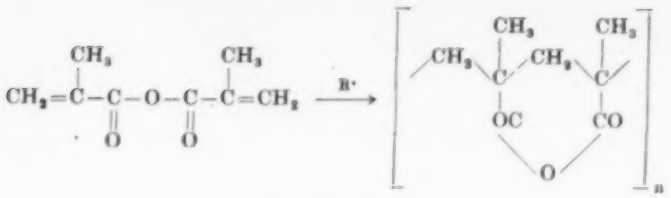
Determination of the nitrogen content of the initial specimen and of the specimen subjected to heating, shows that the amount of nitrogen diminishes in proportion to decomposition from 14·02 per cent (the initial specimen) to 8·33–8·36 per cent (the cyclized specimen) i.e. deamination is accompanied by cyclization. A decrease also occurs in the molecular weight of the polymer.

It has been established by mass spectrometry that in the case of polymethacrylic acid, water is the basic decomposition product. Partial dehydration of polymethacrylic acid to form polymethacrylic anhydride of increased thermal stability can be visualized as taking place according to a scheme such as:



(2)

We have also shown that with cyclic polymerization of methacrylic anhydride under the conditions of Butler's reaction [2], a linear high polymer is formed with a melting point of 200°:



(3)

EXPERIMENTAL

Thermal decomposition of polymethyl methacrylamide and polymethacrylic acid *in vacuo* was carried out on the apparatus already described in [3]. The instrument was calibrated by comparing the actual weight losses of the specimen at the completion of the experiment with those calculated by integration of the kinetic curve measured on a manometer. Obviously this method is accurate only when the composition of the disintegration products is constant.

Deamination of polymethyl methacrylamide was conducted under varying conditions. It was established experimentally that partial deamination of polymethyl methacrylamide *in vacuo* takes place at 310–320°C. After heating for $1^1/_2$ hours a polymer is formed which is soluble in benzene, insoluble in water and with a softening point of—220°C.

Table 1 shows the results of analysing nitrogen content in initial and partially decomposed specimens.

When partial decomposition is conducted in an atmosphere of hydrogen, partial deamination takes place at temperatures 30–40°C lower than in a vacuum, and the cyclized polymer obtained does not gel.

A cyclic polymer of polymethyl methacrylamide is formed not only with thermal decomposition, but also upon heating in aqueous solution at 140°C in sealed tubes in the presence of catalysts, (HBr). Table 2 gives some data on deamination of polymethyl methacrylamide in aqueous solution.

TABLE 1. NITROGEN CONTENT IN THE INITIAL AND PARTIALLY DECOMPOSED SPECIMENS OF POLYMETHYL METHACRYLAMIDE

Decomposition temperature (°C)	Nitrogen content (%)	
	Actual	Calculated
310	8·33	8·37
280	8·34	8·37
280	8·36	8·37
initial specimen	14·02	14·14

The high nitrogen content in the cyclized specimens of polymethyl methacrylamide indicates that under less severe conditions (at 140°C in the presence of HBr) the reaction of deamination and simultaneous cyclization does not reach completion.

TABLE 2. NITROGEN CONTENT IN POLYMETHYL METHACRYLAMIDE SPECIMENS AFTER HEATING THE AQUEOUS SOLUTION AT 140°

Duration of heating (hr)	Cyclized polymer yield (%)	Nitrogen content (%)	
		Actual	Calculated (with complete cyclization)
10	70	12·54	8·37
30	80	10·02	8·37
80	80	10·08	8·37

Polymerization of methacrylic anhydride was carried out in benzene or dimethylformamide with benzoyl peroxide. To an 8% solution of methacrylic anhydride in dry benzene 0·5–1·0% of benzoyl peroxide was added; it was then polymerized in sealed tubes at 50–70°C for 5–20 hr. The polymer of methacrylic anhydride precipitated from the benzene solution, the precipitate was filtered out, washed in ether and dried to a constant weight *in vacuo* at 50°C. The polymer yield was 80–85 per cent. Polymethacrylic anhydride is soluble in dimethyl formamide. The reduced viscosity (η) varied from 0·6–0·8 dl/g depending upon the conditions of polymerization. The specimens of polymethacrylic anhydride have a high softening point (~200°C). They are similar in all respects to the specimens of polymers obtained by partial decomposition (dehydration and cyclization) of of polymethacrylic acid.

CONCLUSIONS

In the process of Partial decomposition of certain polymers of the vinyl series (polymethyl methacrylamide, polymethacrylic acid) give volatile products (methylamine, water) and rings are formed in the primary valence chains. As a result of the latter, thermal stability of the polymers is considerably increased.

Translated by J. J. CORNISH

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INTERNAL ROTATION IN POLYMER CHAINS AND THEIR PHYSICAL PROPERTIES—XVIII. MEAN OPTICAL ANISOTROPY OF ISOTACTIC POLYSTYRENE MOLECULES*

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(*Received* 17 *May* 1959)

A METHOD [1] has been worked out for calculating the mean optical anisotropy of linear polymers of the type $(-CH_2-CR'R''-)_n$, taking into account both the interactions between the adjacent R-groups (which determine the conformations of the monomer units) and also the interactions between the nearest non-adjacent R-groups (which determine the correlation between the conformations of the monomer units). The method is based on the rotational isomer model of the polymer chain suggested by Vol'kenshtein [2].

It was assumed [1] that optical anisotropy of monomer units does not depend upon their conformations. In the case of polymers with massive side chains not possessing axial symmetry, the interaction of the side chains leads to their rotation being dependent upon the rotation of the main chain. Besides this, optical anisotropy of a given monomer unit depends on the relative position of the adjoining monomer units. In the present work, the case will be investigated when the anisotropy of a k-th monomer unit is determined by the conformations of k-th and $(k+1)$ monomer units, i.e. when the rotation of a k-th massive side chain depends on its position relative to $(k-1)$ and $(k+1)$ unit.

METHOD OF CALCULATION

The mean optical anisotropy of the polymer chain can be calculated by the formula in [3]

$$\Delta A = \frac{3}{2} \sum_{k=1}^{n} \left[\sum_{r=1}^{3} \sum_{s=1}^{3} \alpha_{rs}^{(k)} \frac{l'^2}{h^2} \left(\sum_{l=1}^{n} \vec{e}_z^{(l)} \cdot \vec{e}_r^{(k)} \right) \left(\sum_{m=1}^{n} \vec{e}_z^{(m)} \cdot \vec{e}_s^{(k)} \right) - \frac{1}{3} \text{Spur } \alpha^{(k)} \right], \qquad (1)$$

where n is the degree of polymerization; $\alpha_{rs}^{(k)}$ is the component of the tensor of polarizability of a k-th monomer unit; $\vec{e}_r^{(k)}$, $\vec{e}_z^{(1)}$ are unit vectors of local coordinate systems connected with k-th and first monomer units respectively. The z_k axes of these systems are selected so that the sum of the unit vectors $\vec{e}_z^{(k)}$ is directed along a vec-

* Vysokomol. Soedin. **1**: No. 7, 1086–1093, 1959.

tor equal in length to a $\vec{h}$ macromolecule; l' is the length of a monomer unit on axis z. Averaging the composite expression which enters into equation (1) can be reduced, using the method suggested by Gotlib [4], to the averaging of a more simple value differing from that entering (1) by the factor h^2. For this, the averaging of equation (1) is conducted in two stages: firstly for all the conformations of the chain at a fixed chain length h, and then for h. In the first stage, one is set, instead of h, the statistic force $\vec{F}(\vec{h})=(3kT/\bar{h}^2)\vec{h}$ (cf. [5] and [6]) which is regarded as an external force, so that the averaging is conducted for all possible conformations of the chain (including those with different values of h) in the field of the external force. Then we obtain

$$\Delta A=\frac{9}{10}\frac{1}{\bar{h}^2}\left[l'^2\sum_{r=1}^{3}\sum_{s=1}^{3}\sum_{k=1}^{n}\sum_{l=1}^{n}\sum_{m=1}^{n}\overline{\alpha_{rs}^{(k)}(\vec{e}_z^{(l)},\vec{e}_r^{(k)})(\vec{e}_z^{(m)},\vec{e}_s^{(k)})}-\frac{\bar{h}^2}{3}\sum_{k=1}^{n}\mathrm{Spur}\,\alpha^{(k)}\right]. \quad (2)$$

If the polarizability of the monomer units does not depend upon rotation in the primary valence chain, equation (2) passes into equations (1) and (2) of reference [1]. Considering as in [1] the polymer chain with an energy of internal rotation

$$U(\Omega_1,\Omega_2\ldots\Omega_n)=\sum_{i=1}^{n}U(\Omega_{i-1},\Omega_i) \quad (3)$$

Ω_i is the conformation, i.e. an assembly of angles of internal rotation of linkages in the i-th monomer unit), we denote

$$g(\Omega_{i-1},\Omega_i)=e^{-\frac{U(\Omega_{i-1},\Omega_i)}{RT}} \quad (4)$$

In the rotational isomer approximation, $g(\Omega_{i-1},\Omega_i)$ can be considered as elements of the matrix G.

We shall consider, as was mentioned above, that the polarizability of monomer units depends on the conformations in the following manner:

$$\alpha_{rs}^{(k)}=\alpha_{rs}(\Omega_k,\Omega_{k+1}); \quad (5)$$

so that $\alpha_{rs}(\Omega_k,\Omega_{k+1})$ can also be considered as elements of a matrix, whose order f, equal to the order of matrix G, is determined by the number of rotational isomers of the monomer unit.

For calculating the summations with $k>1,m$ which enter into (2), we shall use the hypermatrices $N(r,s)$ and W, which were determined in [1] and constructed so that the matrix of the cosines of the angles of transition between the axes of the i-lst and i-th systems of coordinates $S(\Omega_i)$ is connected with the element $g(\Omega_{i-1},\Omega_i)$ of matrix G. For calculating the summations in equation (2) with $k\leqslant 1,m$ we introduce the hypermatrices $M'(r,s)$ and W', which differ from those considered in work [1] by the fact that in them $S(\Omega_i)$ is connected with $g(\Omega_i,\Omega_{i+1})$. The elements of these hypermatrices are equal to

$$\{M'^{(l-k)}_{(r,s)}\}_{\alpha\beta} = \sum_{\Omega_l}\sum_{\Omega_{l+1}}\cdots\sum_{\Omega_{k+1}} \{U^{-1}\}_{\alpha\Omega_{k+1}} \prod_{i=l}^{k+1} \tilde{S}(\Omega_i) I_{rs} \times$$

$$\times \prod_{i=k+1}^{l} S(\Omega_i)\, g(\Omega_i, \Omega_{i+1}) \{U\}_{\Omega_{l+1},\beta} \tag{6}$$

$$W'_{\alpha\beta} = \frac{\lambda_\beta}{\lambda_1} \sum_{\Omega} \{U^{-1}\}_{\alpha\Omega} \{U\}_{\Omega\beta} S(\Omega). \tag{7}$$

Here $\lambda_1 > \lambda_2 \ldots$ are eigen-values of matrix $G = UAU^{-1}$, $I_{rs} = {}^1/_2 (e_r e_s + e_s e_r)$, the set of three unit vectors $\vec{e}^{(i)}_r$ in the i-th system of coordinates is designated by a column, the tilde signifies transposition, and summation is carried out for all possible conformations of the monomer units. Repeating the transformations which lead to equation (16) in [1], i.e. using the conditions of the cycle of operations ($\Omega_0 = \Omega_n$) and reducing matrix G to the diagonal aspect, for equation (2) we obtain

$$\Delta A = \sum_{r=1}^{3}\sum_{s=1}^{3} S_{rs} [\Gamma(r,s)]_{11} + \frac{9}{10}\frac{l'^2}{\bar{h}^2} \vec{e}_z \sum_{r=1}^{3}\sum_{s=1}^{3} \times$$

$$\times \left\{ \sum_{\alpha=2}^{f} \left[\sum_{k=1}^{n}\sum_{l=1}^{k} N^{(k-l)}_{(r,s)} + 2\sum_{k=2}^{n}\sum_{l=2}^{k}\sum_{m=1}^{l-1} W^{l-m} N^{(k-l)}_{(r,s)} \right]_{1\alpha} [\Gamma(r,s)]_{\alpha 1} + \right.$$

$$+ [\Gamma(r,s)]_{1\alpha} \left[\sum_{l=2}^{n}\sum_{k=1}^{l-1} M'^{(l-k)}_{(r,s)} + 2\sum_{m=2}^{n}\sum_{l=1}^{m-1}\sum_{k=1}^{l} M'^{(l-k)}_{(r,s)} W'^{m-l} \right]_{\alpha 1} +$$

$$+ 2 \left[\sum_{l=3}^{n}\sum_{k=2}^{l-1}\sum_{m=1}^{k-1} (W^{k-m})_{1\alpha} I_{rs} (W'^{l-k})_{\alpha 1} \left([\Gamma(r,s)]_{\alpha\alpha} - \frac{\lambda_\alpha}{\lambda_1} [\Gamma(r,s)]_{11} \right) \right] +$$

$$\left. + 2 \sum_{\substack{\alpha=1 \\ \alpha\neq\beta}}^{f}\sum_{\beta=1}^{f}\sum_{l=3}^{n}\sum_{k=2}^{l-1}\sum_{m=1}^{k-1} (W^{k-m})_{1\alpha} I_{rs} (W'^{(l-k)})_{\beta 1} [\Gamma(r,s)]_{\alpha\beta} \right\} \vec{e}_z , \tag{8}$$

where $S_{r,s}$ are coefficients determined by equations (16) and (25) of [1], and matrix $\Gamma_{(r,s)}$ is connected with component $\alpha_{r,s}$ of the tensor of polarizability of the monomer unit.

$$[\Gamma(r,s)]_{\alpha\beta} = \frac{1}{\lambda_1} \sum_{\Omega_1}\sum_{\Omega_2} \{U^{-1}\}_{\alpha\Omega_1} \alpha_{r,s}(\Omega_1, \Omega_2)\, g(\Omega_1, \Omega_2) \{U\}_{\Omega_2\beta}. \tag{9}$$

When deriving equation (8), it must be taken into account that the spur of the tensor of polarizability of the monomer unit does not depend upon its conformation and consequently

$$\text{Spur}\ \alpha = \text{Spur}\ [\Gamma]_{11} = \sum_{r=1}^{3} [\Gamma(r,r)]_{11}. \tag{10}$$

For carrying out summation in (8), the elements of the hypermatrices $N^{(m)}$ and $M'^{(m)}$ are represented with the aid of recurring equations in the form of a combination of elements of a certain matrix raised to the power m. When this is the case,

equations (21) and (22) of [1] are obtained for the independent elements of the first column of hypermatrix $N^{(m)}$ which are represented in the form of hypervector $\vec{N}^{(m)}$; for the elements of column α we have

$$\vec{N}_{\alpha}^{(m)}(r,s) - R\vec{N}_{\alpha}^{(m-1)}(r,s) + \delta_{r,s}\left(\frac{\lambda_\alpha}{\lambda_1}\right)^{m-1}\vec{L}_\alpha = R^m\vec{N}_{\alpha}^{(0)}(r,s) + \delta_{r,s}\vec{L}_\alpha\frac{\left(\frac{\lambda_\alpha}{\lambda_1}\right)^m I - R^m}{\frac{\lambda_\alpha}{\lambda_1}I - R}, \quad (11)$$

where I is the unit matrix, hypermatrix R was determined in [1], and in the hypervector $\vec{L}_\alpha$ only the component corresponding to the row of number α of the hypermatrix $N^{(m)}(r,s)$ is non zero. A recurring equation for the elements of the rows of hypermatrix $M'^{(m)}$ can be obtained by transposing both sides of equation (11) and substituting the elements of the matrix of the cosines of angles S which enter R for transposed ones. In this case it assumed that the transformation of U is unitary. Substituting equation (11) in equation (8), summing the geometrical progressions and confining oneself to terms of the order n^2 and n (cf the derivation of equation (26) in work [1])we obtain:

$$\Delta A = \sum_{r=1}^{3}\sum_{s=1}^{3} S_{rs}[\Gamma(r,s)]_{11} + \frac{9}{10}\frac{nl'^2}{h^2}\vec{e}_z\sum_{r=1}^{3}\sum_{s=1}^{3}\times$$

$$\times\left\{\sum_{\alpha=2}^{f}(\{-I+2(I-W)^{-1}\}/(I-R)^{-1}\vec{N}^{(0)}/)_{1\alpha}[\Gamma(r,s)]_{\alpha 1} + \right.$$

$$+\sum_{\alpha=2}^{f}(/\vec{M}^{(0)}(I-\tilde{R}(\tilde{S}))^{-1}/\{-I+2(I-W)^{-1}\})_{\alpha 1}[\Gamma(r,s)]_{1\alpha} +$$

$$+2\sum_{\alpha=2}^{f}[W(I-W)^{-1}]_{1\alpha}I_{r,s}[W'(I-W')^{-1}]_{\alpha 1}(\{\Gamma(r,s)\}_{22} - \frac{\lambda_\alpha}{\lambda_1}[\Gamma(r,s)]_{11}) +$$

$$\left.+2\sum_{\substack{\alpha=1\\ \alpha\neq\beta}}^{f}\sum_{\beta=1}^{f}[W(I-W)^{-1}]_{1\alpha}I_{r,s}[W'(I-W')^{-1}]_{\beta 1}[\Gamma(r,s)]_{\alpha\beta}\right\}\vec{e}_z, \quad (12)$$

where $S_{r,s}$ are determined by equation (25) of work [1] and the slanting brackets signify the operation of transferring from vectors $\vec{M}$ and $\vec{N}$ to the corresponding matrices.

We carried out further calculation, as in [1], for isotactic polymers which crystallize in the form of a 3_1 helix and the conformations of the monomer units were determined according to the conformation of the polymer chain in the crystal as suggested by Ptitsyn and Sharonov [7]. According to the conditions of symmetry in solution formulated in [7] there are two *isoenergy* (with an accuracy up to the correlation of the rotations in the adjacent monomer units) rotational isomers of each monomer unit, corresponding to right-handed and left-handed helices, so that $f=2$. For 3_1 helices these rotational isomers are characterized by the pairs of

angles of internal rotation (0·120°) and (−120°,0), and the exact value of 120° can be determined by intermolecular interactions [8]. Therefore we examined the case when monomer units can have conformations $\Omega^{(1)}=(0,\varphi)$ and $\Omega^{(2)}=(-\varphi,0)$.

The method of calculation for this case is described in detail in [1]. We shall note that the summations of the second, third and fifth sums entering equation (12) are only non zero when $r,s=1\cdot2$ and $1\cdot3$, and the summations of the fourth sum are non zero when $r,s=1\cdot1$. Carrying out the calculations we find, if the indices 1 and 2 of the matrix $\Gamma(r,s)$ refer to the conformations $(0,\varphi)$ and $(-\varphi,0)$ respectively

$$\Delta A=\sum_{r=1}^{3} S_{r,r}[\Gamma(r,r)]_{11}+\frac{3}{20}\,\frac{1+p}{p}\,\frac{7+3\cos\alpha}{\sin\alpha}\{[\Gamma(x,z)]_{12}+[\Gamma(x,z)]_{21}\}+$$

$$+\frac{9}{20}\,\frac{(1+p)^2}{p}\left\{[\Gamma(x,x)]_{22}-\frac{1-p}{1+p}[\Gamma(x,x)]_{11}\right\}+ \tag{13}$$

$$+\frac{3}{20}\,\frac{1+p}{\sin\varphi\cos\dfrac{\alpha}{2}}\left[\cos^2\frac{\alpha}{2}(1-\cos\varphi)-2(1+\cos\varphi)\right]\{[\Gamma(x,y)]_{21}-[\Gamma(x,y)]_{12}\}.$$

where coefficients S_{rr} are determined by equations (34)–(36) of work [1], and $p=\sqrt{g_{12}g_{21}/g_{11}}$ is the ratio of probabilities, that two neighbouring monomer units will have different and identical conformations.

The direction of the axes of the local systems of coordinates is shown in the sketch.

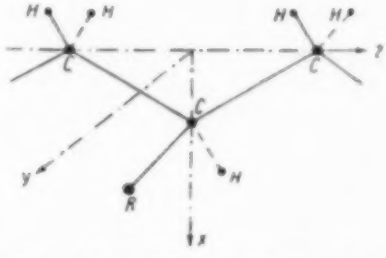

Fig. 1. Local system of co-ordinates.

Substituting in equation (13) the expressions of the elements of matrix $\Gamma(r,s)$ through the components of the tensor of polarizability of the monomer unit following from equation (9), we obtain for the case under investigation

$$\Delta A=\sum_{r=1}^{3} S_{rr}\,\frac{1}{2(1+p)}[\alpha_{rr}^{11}+\alpha_{rr}^{22}+p(\alpha_{rr}^{12}+\alpha_{rr}^{21})]+ \tag{14}$$

$$+\frac{3}{20}\,\frac{7+3\cos\alpha}{p\sin\alpha}[\alpha_{xz}^{11}-\alpha_{xz}^{22}]+\frac{9}{20}[\alpha_{xx}^{11}+\alpha_{xx}^{22}-a_{xx}^{12}-a_{xx}^{21}]+$$

$$+\frac{3}{20}\,\frac{p}{\sin\varphi\cos\dfrac{\alpha}{2}}\left[\cos^2\frac{\alpha}{2}\,(1-\cos\varphi)-2\,(1+\cos\varphi)\right][\alpha_{xy}^{12}-\alpha_{xy}^{21}],$$

where $\alpha_{r,s}^{\alpha\beta}=\alpha_{r,s}(\Omega^{(\alpha)},\ \Omega^{(\beta)})$.

DISCUSSION OF THE RESULTS

As was demonstrated in [1], if angles $\pi-\alpha$ and φ do not greatly differ from $109^0\ 30'$ and 120^0 respectively, then for isotactic polymers having optical anisotropy of the monomer units which does not change with rotation in the main chain

$$\Delta A_0=\sum_{r=1}^{3}S_{rr}\alpha_{rr}=\frac{1}{p}\ \frac{7+3\cos\alpha}{5\sin^2\alpha}\,\Delta\gamma_0\,, \tag{15}$$

where $\Delta_{\gamma 0}$ is the anisotropy of the monomer unit in the principal axes $\xi\eta\zeta$ of the 3_1 helix (axis ζ is the axis of the helix). In this case the component α_{zz} vanishes (cf. equation (5) of work [1]) and

$$\Delta\gamma_0=\alpha_{\zeta\zeta}-\frac{\alpha_{\xi\xi}+\alpha_{\eta\eta}}{2}=-\frac{1}{2}\,\mathrm{Spur}\,\alpha+\frac{3}{2}\left(\alpha_{zz}\cos^2\frac{\alpha}{2}+\alpha_{xx}\sin^2\frac{\alpha}{2}\right). \tag{16}$$

When $\alpha_{xz}\pm 0$ the optical anisotropy of the monomer unit is equal to

$$\Delta\gamma=\Delta\gamma_0\pm\frac{3}{4}\,\alpha_{xz}\sin\alpha\,, \tag{17}$$

where the $+$ and $-$ signs refer to helices with rotational isomers $\ldots 0,\varphi\,;\ 0\varphi\ldots$ and $\ldots -\varphi,0\,;\ -\varphi,0\ldots$, respectively. The equality of all the diagonal components of the tensors of polarizability α^{11} and α^{22}, and the sign difference of components α_{xz}^{11} and α_{xz}^{22}, follows from the fact that helices with rotational isomers $\ldots 0,\varphi\,;$ $0,\varphi\ldots$ and $\ldots -\varphi,0\,;\ -\varphi,0\ldots$ pass one into another when changing the direction of reading.

Since the last summand of the right-hand side of equation (14) vanishes when $\pi-\alpha=109^0\ 30'$ and $\varphi=120^0$, and is small when the values of α and φ are close to the values indicated, it can be neglected. Then equation (14), taking into account equations (15)–(17), can be written in the form

$$\Delta A=\frac{7+3\cos\alpha}{5p\sin^2\alpha}\,\Delta\gamma^{11}-\frac{3}{40}\,\frac{7+3\cos\alpha}{\sin^2\dfrac{\alpha}{2}}\,\delta\alpha_{zz}-\frac{3}{20}\,\frac{2-3\,\dfrac{1-p}{1+p}\cos^2\dfrac{\alpha}{2}}{\cos^2\dfrac{\alpha}{2}}\,\delta\alpha_{xx}\,, \tag{18}$$

where $\Delta\lambda^{11}$ is the anisotropy of the monomer unit belonging to a regular section of the chain (by a regular section of the chain, we mean the totality of two or more monomer units having like conformations), and

$$\delta\alpha_{rr} = \alpha_{rr}^{11} - \frac{1}{2}(\alpha_{rr}^{12} + \alpha_{rr}^{21}) \tag{19}$$

is the difference between the components of the tensors of polarizability of the monomer units, when the conformations of neighbouring monomer units are identical and different. Obviously Spur $\delta\alpha = 0$. Neglecting the small final term in equation (18) we obtain

$$\Delta A = \frac{7 + 3\cos\alpha}{5p\sin^2\alpha}\left[\Delta\gamma^{11} - \frac{3p\cos^2\frac{\alpha}{2}}{2}\delta\alpha_{zz}\right]. \tag{20}$$

The parenthesized expression is the effective anisotropy of the monomer unit, allowing for the contributions of both the regular and irregular sections of the chain; the fractions of the monomer units entering the regular and irregular sections are related as $1:p$. With suffiently large values of p, the main contribution to anisotropy is supplied by the regular sections of a statistically twisted chain. If, in the crystalline chain, the mutual orientation of massive side chains which depends on their rotation is mainly determined by intramolecular, rather than by intermolecular, interactions, then in the regular sections of the chain in solution, the prefferred position of the side chains should be the same as in the crystalline chain. Besides, it stands to reason that in the case of a chain in solution, the side chains can possess greater freedom of rotation than in the crystal.

Let us use formula (20) for comparison with the experimental data. Tsvetkov and Magarik [9], measuring birefringence of isotactic polystyrene, found that the effective anisotropy of the statistical element $\Delta\alpha_{eff}$ is equal to $-220 \cdot 10^{-25}$ cm^3 and consequently, $\Delta A = {}^3/_5\,\Delta\alpha_{eff} = -130 \cdot 10^{-25}$ cm^3. The values of $\Delta\lambda^{11}$ and $\delta\alpha_{zz}$ in the case of polystyrene are equal to

$$\Delta\gamma^{11} = \frac{3}{2}\Delta\alpha_{CC}\left(\cos^2\alpha + \sin^2\frac{\beta}{2}\sin^2\frac{\alpha}{2}\right) - \frac{1}{2}\Delta\alpha_{CH}(1 + 3\cos^2\alpha) -$$

$$- (\alpha_1 - \alpha_2)\frac{1 + 3\cos\alpha}{4} + \frac{3}{2}(\alpha_1 - \alpha_2)\left(\cos^2\frac{\alpha}{2} - \cos^2\frac{\beta}{2}\sin^2\frac{\alpha}{2}\right)\overline{\sin^2\varphi_{11}} -$$

$$- \frac{3}{2}(\alpha_1 - \alpha_2)\sin\alpha\cos\frac{\beta}{2}\,\overline{\sin\varphi_{11}\cos\varphi_{11}} \tag{21}$$

$$\delta\alpha_{zz} = (\alpha_1 - \alpha_2)\left(\overline{\sin^2\varphi_{11}} - \frac{\overline{\sin^2\varphi_{12}} + \overline{\sin^2\varphi_{21}}}{2}\right), \tag{22}$$

respectively, where ψ is the angle of rotation of the benzene ring, read from the plane passing through the bonds CH and C–C_6H_5; the direction of reading ψ is chosen so that with an increase in ψ the perpendicular to the plane of the benzene ring changes from the plane of bonds CH_2–C–CH_2 to the plane formed by bonds

CH_2–C (of the parallel axis ζ) and C–C_6H_5; $(\pi-\beta)/2$ is the angle between the axis x of the local system of coordinates and the bond C–C_6H_5; $\Delta\alpha_{CC}$ and $\Delta\alpha_{CH}$ are anisotropies of bonds C–C and C–H; α_1 and α_2 are the principal polarizabilities of the benzene molecule C_6H_6 in the plane of the ring, and perpendicular to this respectively.

The valence angle $\pi-\alpha$ in the primary valence chain is equal to 116°30′ in the case of polystyrene, [8], [10] and [11]. The value of angle β is unknown, however the calculated value of $\Delta\gamma^{11}$ changes little with varying $\pi-\beta$ within the limits of 109°30′–116°30′. The dehelixation factor of the chain in solution p has already been determined in [12] by comparing theory with the experimental values of the dimensions of isotactic polystyrene molecules.

The following data are available concenring the position of benzene rings in the isotactic crystalline chain. Natta and Corradini [10] believed, from interpreting X-ray diffraction data of isotactic polystyrene, that the perpendicular to the plane of the benzene ring lies in the plane formed by the axis ζ and bond C–C_6H_5, which corresponds to $\psi \simeq 30^0$. A little later Bunn and Howells [11] came to the conclusion, on the basis of a qualitative analysis of the interaction in an individual chain, that energetically the most favourable position of the benzene ring is $\psi=0$. Direct experimental determination of the position of the massive side chain was carried out by Natta and his colleagues [13] in the case of isotactic 1:2-polybutadiene $(-CH_2-CH(CH=CH_2)-)_n$. A study was made of infrared dichroism of the band connected with the vibrations of bond C=C, and it was found that plane CH–CH=CH_2 forms an angle of $\sim 55^0$ with the axis of the chain. This corresponds to an angle of $\psi=0$ and agrees with the model calculations [11].

Thus, when determining the mean values of $\sin^2\psi_{11}$ and $\sin\psi_{11}\cos\psi_{11}$ it can be assumed that benzene rings accomplish torsional vibrations in a certain region $\pm\Delta\psi_1$ near to $\psi_{11}=0$. If one assumes that the difference of the mean square sines which enters into equation (22) is small, so that the term containing $\delta\alpha_{22}$ in equation (20) can be neglected, then a comparison between the experimental value and equation (20) when $\Delta\alpha_{66}=18{\cdot}6\times10^{-25}$ cm^3; $\Delta\alpha_{CH}=2{\cdot}1\times10^{-25}$ cm^3; $\alpha_1-\alpha_2=59{\cdot}6\times10^{-25}$ cm^3 [14], [15] leads to a value of $\Delta\psi_1\approx30^0$.

Allowance for the difference of the mean squares of the sines for the regular and irregular sections of the chain (cf. equations (20), (22)) leads to an additional parameter. Comparing equation (20) with the experimental value ΔA we find that the half width of the interval $\Delta\psi_1$ can lie within the limits of 0 to 60°, whereas $\frac{1}{2}(\sin^2\psi_{12}+\sin^2\psi 21)$ can have a value of from $\frac{1}{4}$ to 0 respectively. If the benzene rings of the irregular sections of the chain also vibrate about $\psi=0$ in the interval with half width $\Delta\psi_2$ we get $\Delta\psi_1+\Delta\psi_2\simeq60^0$. For choosing between the possibilities which have been demonstrated, it is necessary to have experimental data on the dipole moments and optical anisotropy of the substitution derivates of isotactic polystyrene.

In conclusion the authors wish to express their sincere gratitude to M. V. Vol'kenshtein and O. B. Ptitsyn for discussing the results of the work.

CONCLUSIONS

(1) The dependence of rotation of side chains on rotation of the main chain substantially effects the optical anisotropy of the chain.

(2) In the case when rotation in the macromolecule is greatly retarded, the mean anisotropy of the macromolecule is proportional to the anisotropy of the regular twisted sections of the chain.

(3) For isotactic polystyrene, the irregular sections of the chain can also supply a marked contribution to anisotropy.

Translated by J. J. CORNISH

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CONCERNING TWO CRYSTALLINE MODIFICATIONS OF 1,4-*TRANS*-POLYBUTADIENE*

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(*Received* 19 *May* 1959)

IT was shown recently that regularly constructed crystallizable polymers of the 1,2 dienes can be formed with the aid of heterogeneous catalysts. The 1,4-*trans* polymers obtained under these conditions are characterized by structural regularity and have an almost totally linear structure, consisting of 1,4-*trans* links.

In work [1] a polybutadiene was obtained whose crystallinity, determined by the x-ray diffraction method reached 70–75%. Analysis by infra-red absorption spectra showed that this polymer consisted basically of *trans*-1,4 links with a small content of 1,2-links. In this case, the *cis* configuration of 1,4 was almost entirely absent. Crystalline polybutadiene has a high density, near to unity. As follows from work [1], 1,4-*trans* polybutadiene can exist in two crystalline modifications.

In work [2] a study was made of the temperature dependence of the deformation rate of polybutadiene under the action of a continuous compressive stress. The curves obtained are characterized by two maxima. The first maximum, corresponding to a temperature of 75–80°C, was referred by the authors to the melting point of defective crystals. The second maximum (the biggest in size), corresponding to a temperature of 125–140°C, is connected with the melting point of the more regular crystals. In the present work, a study was made of 1,4-*trans* polybutadiene, obtained by the method described in work [2]. Roentgenograms were taken of polybutadiene, and the infra-red absorption spectrum was studied in the temperature interval +20–+150°C.

X-RAY DIFFRACTION STUDY OF POLYBUTADIENE

Roentgenograms of the specimens were taken on a unit type URS-501, which registered scattered radiation by means of a Geiger Counter. We used K_α-radiation of copper, released by a nickel filter. Specimens were prepared in the form of pellets by compacting the polymer at room temperature. When obtaining the curves for x-ray scattering, the specimens were heated from two sides by

* Vysokomol. soedin. 1: No. 7, 1094–1099, 1959.

a special electric oven. The temperature was determined and maintained with an accuracy of $\pm 2°$, using a thermocouple connected to a thermocontrol instrument EPV-01. Figure 1 shows x-ray scattering curves for polybutadiene specimens obtained at different temperatures. It can be seen from Fig. 1 that when angle $2\vartheta = 22{\cdot}5°$, a well defined peak is observed at 20°, which characterizes crystalline modification No. I. At 55° the intensity of this peak diminishes, and a second peak appears simultaneously when $2\vartheta = 20{\cdot}8°$, which indicates the

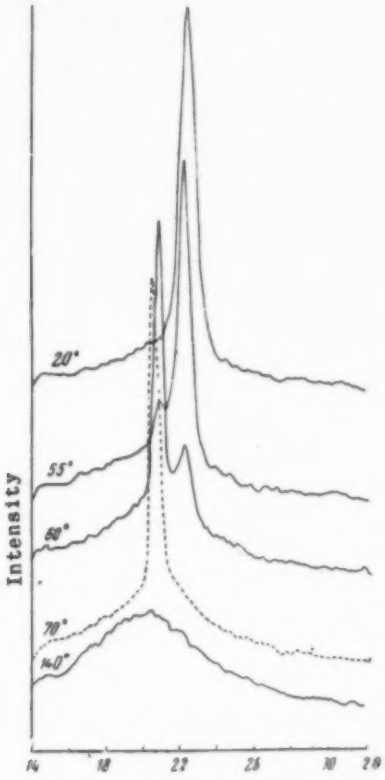

FIG. 1. Curves for x-ray scattering for a specimen of polybutadiene at various temperatures (°C).

occurrence of the second crystalline modification, No. 2. The intensity of the second peak grows with increasing temperature, while the intensity of the first peak drops. At 70°C the first peak completely disappears, i.e. a permanent transition of modification 1 into modification 2 takes place. Further heating is accompanied by a decrease in the intensity of the peak at $2\vartheta = 20.8$°C, which is

connected with the melting of the crystals of modification 2. At 135°C the crystalline peak completely disappears, and scattering by the amorphous part is observed when $2\vartheta = 20°C$.

The crystallinity of modifications 1 and 2 was determined as a percentage at different temperatures by comparing the integral intensities of the scattering from the crystalline and amorphous parts, using the method developed for polyethylene in work [3]. The percentage of crystallinity was calculated by the formula given below:

$$K = \frac{I_{k\,I,\,II}}{I_k + 0{\cdot}7I_A} \times 100\%,$$

where $I_k = I_{k,I} + I_{k,II}$, and $I_{k,I,II} = I_{k,I}$ or $I_{k,II}$ $I_{k,I}$ and $I_{k,II}$ respectively are integral intensities of the peaks of crystalline modifications 1 and 2; 0·7 is the coefficient, allowing for the angular position of the diffraction maxima of the crystalline and amorphous parts. The integral intensities were determined by weighing the area of the peaks copied on to tracing paper. The results obtained, and a comparison between them and the data from infra-red spectroscopy, are given in Table 1.

TABLE 1. CRYSTALLINE CONTENT DEPENDING ON TEMPERATURE

Temperature (°C)	Per cent of crystallization				Temperature (°C)	Per cent of crystallization			
	X-ray diffraction			by IK-spectra C_{cryst}		X-ray diffraction			by IK-spectra C_{cryst}
	K_I	K_{II}	$K=(K_I+K_{II})$			K_I	K_{II}	$K=(K_I+K_{II})$	
20	79	—	79	75	70	—	54	54	46
50	74	—	74	69	80	—	42	42	40
55	66	7	73	67	100	—	21	21	35
60	24	41	65	60	135	—	—	0	0

As can be seen from the Table, the percentage of crystallinity for modification 1 at 20°C is 79 per cent according to x-ray diffraction data. With complete transition of modification 1 into modification 2, which takes place at 70°C (cf. Fig. 1), the percentage of crystallinity is 54. Thus, this transition is accompanied by a decrease in the crystalline part of the polymer.

When cooling a specimen previously heated to 140°C a reverse transition, of modification 2 into modification 1, is observed; this demonstrates the stability of modification 1 at room temperature. We attempted to fix the amorphous structure or crystalline modification 2 by rapidly cooling a heated specimen, but modification 1 was obtained every time. By determining the scattering angles 2ϑ corresponding to modifications 1 and 2, it was shown that their values when heating the specimen to melting point are different from their values when

subsequently cooling, at one and the same temperature. The data obtained are given in Table 2.

TABLE 2. CHANGE IN THE SCATTERING ANGLES WHEN COOLING THE SPECIMEN

Temperature (°C)	$2\vartheta_I$		$2\vartheta_{II}$	
	heating	cooling	heating	cooling
20	22°28′	22°48′	—	—
50	22°14′	22°44′	—	—
55	22°14′	22°42′	20°54′	21°20′
60	22°14′	22°40′	20°54′	21°18′
70	—	—	20°48′	21°14′
80	—	—	20°51′	21°6′
100	—	—	20°36′	21°4′

As can be seen from Table 2, angles 2ϑ increase when cooling a previously heated specimen. Repeated heating and cooling (2nd and 3rd cycles) only lead to an insignificant increase in these angles. The increase observed in angles 2ϑ, corresponding to a decrease in interplanar spacings, can be explained by better packing of the molecular chains in the crystalline regions of the polymer.

INFRA-RED ABSORPTION SPECTRUM OF POLYBUTADIENE

Absorption spectra were obtained both on a single-ray instrument and on a double-ray one (IKS-14) with a NaCl prism. The specimens were prepared by melting polybutadiene between two NaCl plates, or by compacting between foil, and heating to 160°C. When registering the spectra at different temperatures, special ovens were employed, between which the two plates of NaCl containing the specimen were placed. In one of the plates there was a hole for the thermocouple with which the temperature of the heated specimen was determined.

Figure 2 shows the absorption spectrum for crystalline polybutadiene. This spectrum practically corresponds to the spectrum for polybutadiene obtained in work [1]. The intense band 10·30 μ in Fig. 2 characterizes 1,4-*trans*, the weak bands 10·96 and 13·60 μ refer to 1,2- and *cis*-1,4 configurations. Thus, the specimen which we were studying was mainly composed of 1,4-*trans* links. It was established in work [1] that the three very intense bands 12·93, 9·49 and 8·10 μ, and also the weakest bands 8·92 and 7·49 μ are "crystalline" in as much as they disappear when polybutadiene is dissolved.

At the present time there is no well defined answer to the question of the physical cause of the formation of crystalline bands. However, these bands can definitely be considered to occur as a result of the ordered spatial arrangement

of the sections of the chains forming the crystal lattice. The appearance of crystalline bands can be explained in a number of cases by interaction between the vibrations of neighbouring groups in the crystalline region [4,5]. We made a detailed study of the temperature dependence of crystalline bands 12·95,

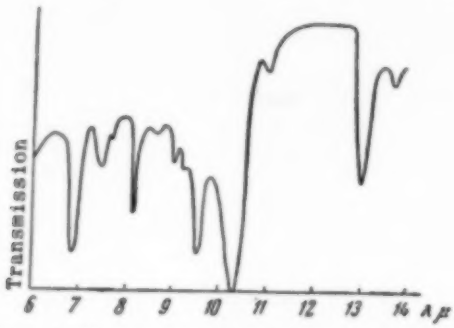

Fig. 2. IR-spectrum of polybutadiene at 20°.

9·50 and 8·10 μ. Figure 3 shows the dependence of optical density on temperature for these bands. It can be seen from Fig. 3 that, starting from $t \approx 55$°C all three bands have diminished intensity, which corresponds to the temperature at which modification I begins to melt. At $t \approx 70$°C the melting process of this modification ceases. This corresponds to the second hump in the curves. The result obtained agrees with the x-ray diffraction studies set forth above, which showed that at this temperature complete transition of modification I into modification II takes place. Band 8·10 μ, which undergoes a second change

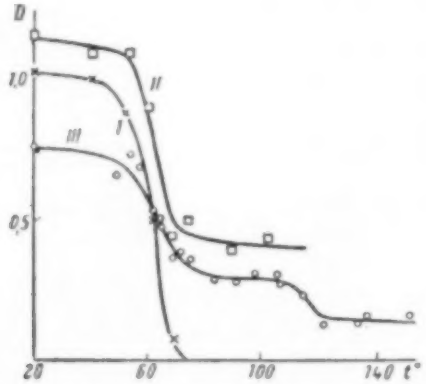

Fig. 3. Optical variation in density of "crystalline" zone with temperature. (I) Zone 12·95 μ (II) Zone 9·50 μ (III) Zone 8·10 μ.

in optical density in the temperature range 110–130°C (cf. Fig. 3), is of particular interest. This change is connected with the melting of modification II. Thus,

band 8·10 μ is a complex band and characterizes both modification I and II. These two modifications are probably characterized by close frequencies (as was observed, for example, in the case of gutta percha [6]) which were not allowed by the instrument in our case.

By using the crystalline absorption bands, one can determine what part of the polymer is crystalline; however in this case one must have a standard specimen with a known crystallinity content. These data can be obtained for the standard specimen, as we have seen, from x-ray diffraction studies.

An independent method of determining crystallinity is to study the temperature dependence of absorption in the so called "amorphous" bands. This method was first used for polyethylene [7]. An increase in optical density is typical for the amorphous bands when the crystalline part of the polymer melts. Probably these bands characterize definite vibrations of groups in the rotational isomer which exists in the amorphous part. Such absorption bands for 1,4-*trans* butadiene are 7·65 and 7·43 μ. Below a temperature of ~ 65°C the latter band is complex, due to the intense crystalline band 7·49 μ being superimposed on it, this however disappears at temperatures higher than this.

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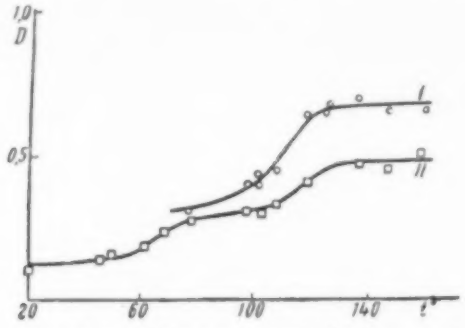

Fig. 4. Optical variation of density of amorphous zone with temperature. (I) Zone 7·43 μ (II) Zone 7·65 μ.

Figure 4 shows the dependence of optical density on temperature for amorphous bands. As can be seen from a comparison of the curves in Fig. 3 and 4, optical densities for bands 7·65 and 8·10 μ change with temperature in the opposite direction, which is connected with the transition of the crystalline part into amorphous. At 50–70°C optical density of the 7·65 μ band considerably increases; this corresponds to the temperature range in which crystalline modification 1 melts. The second significant change in the optical density of the 7·65 μ band is observed in the temperature range 110–130°C. This corresponds to the temperature range in which modification 2 melts. Above 130°C the polymer goes over entirely to the amorphous state, and the concentration of the amorphous part C_a is unity. As in the case of polyethylene in work [7], we made use of this circumstance to determine what percentage of the polymer was crystalline

and what amorphous. At temperatures above 130°C the optical density of the 7·65 μ band is equal to:

$$D_1 = \varepsilon c_a d, \tag{2}$$

where ε is the absorption factor, and d is the thickness of the layer. At $t \leqslant 130$°C the optical density is

$$D_2 = \varepsilon c'_a d. \tag{3}$$

From equations (2) and (3), knowing that $C_a = 1$, we shall obtain $C_a = D_2/D_1$, and the concentration of the crystalline part per cent at a temperature t equals: $C_{cryst} = (1 - C'_a) \cdot 100$. The results obtained for different temperatures are set forth in Table 1. Comparison of the x-ray diffraction data and the data obtained by the spectroscopic method are in good agreement.

CONCLUSIONS

(1) The temperature dependence of the degree of crystallinity of 1,4-*trans* polybutadiene was studied by x-ray diffraction and infra-red spectroscopy. The melting temperatures of two crystalline modifications were determined.

(2) It was established that at a temperature of ~ 70°C a complete transition takes place in 1,4-*trans* polybutadiene of modification I into modification II, and the degree of crystallinity of modification II is lower than that of modification I. In the temperature range 55–70°C both these crystalline modifications exist.

(3) It was shown that modification I is stable at room temperature.

(4) The values of the scattering angles 2ϑ corresponding to the crystalline peaks of modifications I and II are different when heating and cooling the specimen. It has been proposed that the increase in these angles when cooling is connected with improved packing of the molecular chains in the crystal cell.

Translated by J. J. CORNISH

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THE VIII MENDELEYEV CONGRESS AND POLYMER SCIENCE IN THE U.S.S.R.*

G. L. Slonimskii and P. V. Kozlov

The VIII Mendeleyev Congress on general and applied chemistry, which took place in Moscow from 16 to 23 March 1959, was a great event, not only in the lives of Soviet chemists, but in the lives of the entire scientific and technical community of our country. Furthermore, the fact that a large group of famous chemists from a number of foreign countries participated in the work of the congress, made it a great event in the lives of the international community of chemists. The grandiose scale of the Mendeleyev Congress is illustrated by the following data: apart from the plenary sessions, at which 11 papers were read by the greatest scientists of our country, the work of the congress was carried on in seventeen sections, as well as at a Symposium on higher chemical and technological education and at a Commission on chemical nomenclature. At these meetings 1373 reports and communications were made by 2058 authors. Over 5000 scientists, engineers and workers of the chemical industry took part in the work of the congress.

Twenty-five years have passed since the previous—the VII—Mendeleyev Congress was convened. What a vast expansion in Soviet chemistry there has been since then. How vigorous has been the rise of the Soviet chemical industry. Overall production by the chemical industry is 21 times greater in 1959 than it was in 1934. Great are the tasks set by the XXI Congress of the CPSU for the developed construction of a communist society, in which special attention is paid to the further, accelerated development of the chemical industry; tasks, which after the May 1958 Plenum of the Central Committee of the CPSU, became a national matter. Convened at a time when the Soviet people had actually begun to carry out the historical decisions of the XXI Extra-ordinary Congress of the CPSU, the Mendeleyev Congress reviewed the state of Soviet chemical science and set the course for further research and for putting the achievements of chemical science into practice.

The VIII Mendeleyev Congress began its work in the Assembly Hall of Moscow University with an introductory speech by the Chairman of the Organizing Committee—President of the Academy of Sciences U.S.S.R, Academician A. N. Nesmeianov, who stressed the significance of the congress for developing Soviet chemistry, and the tasks which confront it in the light of the decisions made by the XXI Extra-ordinary Congress of the CPSU.

Great attention was paid in the work of the VIII Mendeleyev Congress to one of the youngest branches of chemical knowledge—polymer science, and to its applications.

In a number of reports at the plenary sessions of the congress and in the reports and communications at the majority of sections, particularly in the section dealing with the chemistry and technology of polymers, undoubted successes in the field of polymer science were demonstrated, and new tasks were set for developing this science. On the opening day of the congress, two reports were mainly devoted to the state of polymer science and the polymer industry. The report by V. S. Fedorov, Chairman of the State Committee for Chemistry of

* Vysokomol. Soedin. 1: No. 7, 1112-1125, 1959.

the Council of Ministers USSR, on the tasks of scientific and technical progress in the chemical industry; and the report by Academician V. A. Kargin on the basic problems of polymer chemistry.

In his report, Fedorov reviewed the state of the whole of chemical science and the chemical industry, recalling the tasks which confront the latter in the light of the decisions made by the May 1958 Plenum of the Central Committee of the CPSU, and the decrees made by the decrees made by the XXI Extra-ordinary Congress of the CPSU. Having presented the basic data of the Seven Year Plan for the development of the national economy of the U.S.S.R as regards the chemical industry, Fedorov dwelt particularly on the main features which are characteristic of this new period in the development of the Soviet chemical industry. The principal feature is the all out, accelerated development of the production of polymer materials. The output of artificial fibres is to be increased four times, and the most valuable of these—synthetic fibres—12–14 times. Production of plastics materials and synthetic resins must be increased by more than 7 times, including the production of phenol formaldehyde resins by $3^1/_2$ times, and carbamide resins by 12 times. The production of acetyl cellulose plastics, which are the initial raw material for acetate rayon, and of incombustible acetate films must be increased by more than 18 times. Production of polystyrene, ftoroplasts,* polyamide plastics, polyacrylic and other polymers is greatly increasing. The powerful production base for manufacturing polyethylene and polypropylene, both of which are of great importance in many sections of the national economy, and for fabricating a variety of articles for everyday life, is being almost recreated. In this period of development in the chemical industry, there is a significant increase in the variety of synthetic rubbers whose production is based on new synthetic resources of raw material. Such hitherto unseen scales and rates of development of polymer materials will require, as Fedorov stressed, a great increase in scientific research and in technological, design and projecting works which must assure the accelerated development of the Soviet polymer industry.

In his paper about the basic problems of the chemistry of polymers, which was heard with great interest by the participants in the congress, Academician Kargin described in short the history of the emergence and growth of polymer science, gave a general analysis of its present day state, but devoted the main part of his report to the basic scientific problems confronting this vigorously developing branch of chemical knowledge. The first of these problems is the whole complex of work connected with obtaining polymers which can be used in the widest possible temperature range, understanding by temperature range the difference between the temperature of the onset of flow or chemical decay and embrittlement temperature. Kargin stressed that a number of modern technical fields, in first place aircraft construction, rockets and the electrical industry, require polymer materials which can be used at temperatures of 300–400° and over. Therefore the synthesis of new polymer substances resistant to thermal and oxidative decay is one of the basic trends in the field of polymer chemistry. The second problem, in the opinion of the speaker, which is insistently being put forward by practice, is the creation of new polymer substances, distinguished not only by improved qualities but by increased cheapness and availability. The solution of this problem is connected with both prospecting in the field of synthesis for new polymers from more available raw material, as well as with the search for new methods and procedures for polymerizing known monomers. Finally, the third urgent task confronting polymer science is the solution of a group of problems connected with the conversion of polymers to useful articles.

In the light of these problems, Kargin dwelt in detail on trends in the search for new monomers, on polymerization processes and, in particular, on processes for obtaining block and graft polymers and on concrete questions of developing a general theory connecting the composition and structure of polymer chains with the properties of polymers.

* *Translator's note.* Literally, fluoroplastics.

In this report, independent significance was attached to a review of the problems connected with creating inorganic polymers, particularly with obtaining polymeric electrolytes, as well as with their properties. The development of work in the field of polyelectrolytes, as Kargin pointed out, is extremely important, not only for solving a number of practical problems, but it also promises much in the matter of simulating biological processes, which will be of undoubted advantage in the development of our concepts of these processes.

The development of the works mentioned above on the one hand, and a thorough study of natural high-molecular compounds which are of paramount importance in explaining functions of life with living organisms on the other hand, determine the present state and progress of physico-chemical biology, a principal section of which is biochemistry.

To this fascinating field of chemical knowledge Academician V. A. Engel'gardt devoted his report, which was heard with great interest at one of the plenary sessions by the participants in the Mendeleyev Congress. In this paper, on some of the problems of modern biochemistry, Engel'gardt stated that of all the sections of modern chemistry, biochemistry is the one which is undergoing particularly vigorous and precipitate growth. It can be placed only on a line with the chemistry of synthetic polymers which in recent years has occupied the most prominent place in chemical science. In the same way in modern biochemistry as well, the most prominent attention is being concentrated on the study of two classes of natural high-molecular compounds: the albumins and the nucleic acids.

Engel'gardt dwelt shortly on modern concepts of the constitution and structure of nucleic acids, first of all on desoxyribonucleic acid, as a concerete chemical substance which accomplishes the transmission of hereditary information in a series of generations, and also on general concepts of the possible mechanism of mutation processes accomplished quantitatively by radiation or chemical action. In spite of the successes achieved in the field of studying nucleic acids, the next most important problem is to decipher the sequence in which nucleotidal links are arranged in the vast nucleic acid chain. This extremely difficult problem, as Engel'gardt emphasized, can in all probability be solved successfully by the invention of principally new procedures for analysing the structure of nucleic acids.

A great part of the report was devoted to modern concepts of albumen synthesis which takes place under the control of, and with the close assistance of ribonucleic acid. At the present time it is possible to divide the process for synthesizing the albumen molecule into a series of isolated and clearly defined stages: the activation of amino acids, followed by the ordered combination of these activated amino acids, i.e. the formation of an albumen molecule and the occurrence of a definite, specific for the particular albumen, three dimensional arrangement; in other words, the occurrence of a volume structure. The lecturer threw light upon recent experimental data accumulated by researches concerning the mechanism by which all these stages take place in a living organism. Although the initial stages of albumen synthesis have been studied in some detail, the closer we approach the final stages of this synthesis, the more we are convinced of the inadequacy of our knowledge concerning the actual chemical mechanisms.

The lecturer went on to give a general review of data accumulated on problems connected with studying the chemical nature of a number of albuminous bodies, of the synthesis of certain of them and of the part played by individual types of albumen in the manifestation of vital functions in living organisms. It is precisely these questions, concerning the connections and dependences between the chemical structure and biological functions of the biologically active high-molecular substances of a living organism, which are among the radical problems of biochemistry. In some of these substances it has been possible to isolate those portions or chemical groups which are responsible for the development of biologically active properties in the given albumen as a whole. Finally, the extension of biochemistry to include the field of disruptions of individual functions of an organism which lead to illness, makes it possible to interpret the nature of a given illness by an understanding of the chemical

changes which have taken place in the molecular structure, of the interactions between chemical substances or by an understanding of the chemical reactions caused by ferments. Research in this field has made it possible to establish the new science of "molecular diseases", which are a result of definite chemical changes in the molecular structure of biologically active substances and in the first place, of albumens. The lecturer detailed examples of diseases such as these. In conclusion, Engel'gardt the attention of those taking part in the congress to the great significance of "functional biochemistry," which is called upon to give a biochemical, which in the end means a chemical interpretation of the nature, mechanism and substance of certain physiological functions. In the opinion of the lecturer, this will be the basic and main objective of the biochemistry of the future.

The reports by Kargin and Engel'gardt were devoted wholly to high-molecular chemistry—the first, to general questions of polymer science, and the other, to problems of biologically important natural high-molecular compounds as well as to some aspects of the application of a knowledge of these compounds in biology—but a number of other reports heard at the plenary sessions of the congress dealt to a greater or lesser degree with the individual branches of polymer science and its applications.

Thus, in the paper by N. N. Semenov on the basic problems of chemical kinetics, a detailed explanation was given of the rôle of free radicals, which play a basic part in chain reactions to which, as is known, the processes of radical polymerization of monomers belongs. Now these processes are the basic processes of polymer synthesis. At the end of his report, Academician Semenov spoke of the most recent work carried out at the Institute of Chemical Physics and in the Laboratory of Anisotropic Structures, on studying free radicals occurring in the process of polymer synthesis and in the process of interaction between certain nucleic acids and albuminous compounds.

In the report by Academician A. P. Aleksandrov on the chemical aspects of the application of atomic energy, individual problems of the application of atomic energy in the synthesis and treatment of polymers were reflected. The great discovery of human genius—mastering the forces of the atomic nucleus—gives not only a powerful source of energy, but media which are completely exceptional in their efficiency for accomplishing a variety of chemical transmutations. This is an extremely promising and advantageous sphere for the application of nuclear energy. Thus for example, the radiant energy of the nuclear fuel exhausted by only one of the atomic power stations being constructed in the U.S.S.R., could be used for vulcanizing hundreds and thousands of tyres and producing huge quantities of polyethylene. Radiochemistry opens up new possibilities for intensifying and making cheaper the processing of a number of important products, including polymers with pre-assigned qualities, such as graft and block polymers. The application of atomic energy for bringing about chemical reactions is at the present time, as Aleksandrov emphasized, still in its infancy; but this branch of chemistry holds great prospects for rapid and successful development.

The results of original work in the field of polymer science were heard in speeches given at a number of sections, but mostly in the section dealing with the chemistry and technology of polymers.

At the sessions of this section alone, which lasted for several days, 84 reports and communications were heard, devoted to a very wide circle of questions on the chemistry, physics and technology of high-molecular compounds. We shall not stop in this survey on the reports and communications made in the sections for organic chemistry and technology, which referred to such low-molecular organic compounds as the initial products (monomers) for forming high-molecular substances.

A great part of the reports and communications heard in the section for the chemistry and technology of polymers referred to the synthesis of new types of polymers, the development of new methods of synthesis and the modifications of the properties of polymers.

The report by I. P. Losev and L. A. Datskevich (Moscow Chemicotechnological Institute i/n D. I. Mendeleyev) summed up work on the synthesis and properties of polyester urethanes i.e. the products of the interaction between di*iso*cyanate and polyesters. By studying the properties of a great number of new polymers, it was found possible to obtain elastic and tough polyester urethanes, and the general laws have been found for the dependence of the mechanical properties of these polymers on the molecular weight. Technically valuable films have also been prepared.

V. V. Korshak, S. L. Sosin and M. V. Christiakova (Institute of Elemental Organic Compounds of the Academy of Sciences, U.S.S.R. Moscow) reported on an interesting new method of obtaining high-molecular compounds by means of a reaction which they have called 'polyrecombination'. By employing the reactions between free radicals and saturated compounds, it was found possible to form linear polymers. Polydi*iso*propyl benzene (mol. wt. 10,000) was obtained, as well as a number of other polymers, by decomposing tributyl peroxide dissolved in *n*-di*iso*propyl benzene, *n*-xylene, di*iso*propyl ketone, di*iso*propyl ferrocene, diphenyl etc. Detailed data were given in the report about the new polyrecombination reaction, and also about the properties of polymers obtained by this method.

Ye. V. Kuznetsov (Kazan' Chemicotechnological Institute i/n S. M. Kirov)presented the results of work on the synthesis of copolymers of the system: unsaturated ether–unsaturated acid–salt of unsaturated acid. Data were submitted, showing the influence exerted by the nature of the metal forming the salt on the rate and degree of polymerization. Data were also given on the properties of these copolymers. It is interesting to note that by forming the corresponding salts, it is possible to introduce radioactive isotopes of a metal into polymers. The radioactive plastics obtained, were tested as therapeutic preparations, radiation standards, pulse transmitters and as a medium for the prevention of static electricity. Other promising applications of copolymers containing unsaturated acid salts, is their use as ionogenetic resins, synthetic detergents, catylists and regulators for polymerization processes. It was also found that copolymers of methyl methacrylate, methacrylic acid and methacrylic acid salts can find an application as filters for various electromagnetic radiations.

Information was given in the paper by A. A. Vansheidt and N. N. Kuznetsova (Institute of High-Molecular Compounds of the Academy of Sciences, USSR, Leningrad) on the synthesis of weak acid ion-exchange resins, based on polycondensation of phenoxy acetic acid with formaldehyde. The resins are distinguished by high selective capacity to streptomycin and a number of other large organic ions. F. T. Shostak (Plastics Materials Works, Nizhnii Tagil) told of the synthesis of new, high quality ion-exchange resins by condensation of sulphonated naphthalene with formaldehyde, and also of a mixture of sulphonic acids, naphthalene and phenol.

A large number of communications was devoted to new methods of synthesizing various polymers, to the study of the mechanism of the reactions of polymer formation, to the influence of various factors of reaction rates of polymer formation and on the physical properties of the polymers obtained. The following refer to works such as these: copolymerization of unsaturated polyesters with vinyl monomers (S. S. Spasskii, A. V. Tokarev, M. A. Mikhailov, A. I. Tarasov, T. V. Molchanova and M. Ye. Mat'kova —Institute of Chemistry, Urals Branch of the Academy of Sciences, USSR, Sverdlovsk) leading to the formation of graft polymers, employed in the production of reinforced plastics; the formation of phenol-oxazolidine resins, which proved to be of technical interest (K. D. Petrov, O. K. Gosteva and V. I. Pukhova – State Scientific Research Institute of the Plastics Industry, Moscow); copolymerization of acrylonitrile with esters of vinyl sulphonic acid and amides of acrylic and methacrylic acids (V. S. Diurnbaum, with A. D. Abkin and V. S. Klimenkov – All-Union Scientific Research Institute for Artificial Fibres, Mytishchi) which led to the formation of valuable fibre-forming polymers; synthesis of polyamides from *ω*-ami-

noalkyl phenyl alkannic acids (M. N. Bogdanov, with G. I. Kudriavtsev—Scientific Research Institute for Artificial Fibres, Mytishchi); polymerization of the salts of acrylic and methacrylic acids in the presence of other solid salts (G. P. Andrianova, with V. A. Kargin and V. A. Kabanov—Moscow State University i/n M. V. Lomonosov); study of the influence of sodium salts of the fatty acids on the kinetics of polymerization of styrene in emulsion (S. S. Ivanchov—L'vov State University i/n I. Franko); formation of graft polymers by chemical synthesis methods (A. S. Daniushevskii, with A. F. Vorob'yeva—Scientific Research Institute of Plastics, Moscow); research into the mechanism of setting phenol formaldehyde lacquer resins with hexamethylene tetramine (L. A. Igonin, with M. S. Akutin and V. A. Kargin—Scientific Research Institute of Plastics, Moscow).

Special attention should be paid to the report by S. I. Sokolov, with N. A. Shchegolevskaia (Moscow Institute of Chemical Machine Building) on the synthesis and photoelastic properties of a number of new polymers, for which connections were discovered between composition and optical activity using birefringence, which is of significance for the development of the polarization—optical method of investigating stresses in polymers. Attention should also be paid to the report on the work carried out by V. P. Zubov with V. A. Kargin and V. A. Kabanov (Moscow State University) on an original method of polymerization in systems obtained by the molecular beam method, when the components were mixed by simultaneous evaporation *in vacuo* and condensation on a surface cooled by liquid nitrogen. The polymerization process which takes place when such a system thaws out, differs both from polymerization processes taking place in homogeneous systems and from heterogeneous polymerization processes.

K. A. Andrianov (Institute of Elemental Organic Compounds of the Academy of Sciences, U.S.S.R., Moscow) reported on the synthesis of a new class of polymers whose molecular chains are constructed from atoms of silicon, oxygen and aluminium—polyorganoalumosiloxanes. Data were given in the report, on methods of obtaining such polymers, and on their main physical properties.

A. A. Zhdanov, with K. A. Andrianov (Institute of Elemental Organic Compounds) reported on obtaining polyorganosiloxanoalumoxanes. These polymers, which are hard resins, are soluble in organic solvents, and are convertible under certain conditions into an infusible and insoluble state; they do not contain silicon atoms in their pricnipal molecular chain, but only in the groups encompassing the chain. It is also possible to obtain polyorganosiloxanotitanoxanes and polyorganosiloxanostannoxanes.

In the report by Z. N. Nudel'man, A. S. Novikov and K. F. Kaluzhenina (Scientific Research Institute of the Rubber Industry, Moscow), results were given of a study of the interaction between siloxanes and organometallic compounds, on the basis of which a simpler method than the existing one was worked out for vulcanizing silicone rubber without using peroxides.

N. A. Glukhov (Institute of High-Molecular Compounds, Leningrad) reported on the synthesis of polymeric, organometallic chelate compounds based on the interaction between tetraketones and acetyl acetonates of zinc, magnesium, copper, nickel, cobalt, beryllium and other metals. The synthesized polymers have a melting point from 250° to 380°C and are characteristically heat resisting.

V. A. Krol', B. D. Babitskii, I. I. Boldyreva, L. S. Bresler, B. M. Volovik, L. A. Gavrilova and B. A. Dolgoplosk (All-Union Scientific Research Institute of Synthetic Rubber i/n S. V. Lebed'yev, Leningrad) reported on a study of the interaction between titanium halides and organoaluminium compounds, they also told of the dependence of the structure of polydienes upon the composition of the catalytic mass. It was shown that titanium halides are reduced by organoaluminium compounds even as far as metallic titanium, also that the reduction process goes deepest when using triethyl aluminium. Carrying out polymerization of isoprene and butadiene with the aid of similar kinds of catalytic mass, has made it possible

to find connections between the structure of corresponding polydienes and the character of the catalytic mass, and also to study the chemical changes in the catalytic mass in the process of polymerization. By using different catalytic masses, it was possible to form polyisoprene containing up to 95 per cent *cis*-1,4 links, polyisoprene containing up to 98 per cent *trans*-1,4 links and polybutadiene containing up to 98 per cent of 1,4 links. The latter polymer vitrifies at −105°C and contains a considerable amount of crystalline regions.

Research into the reactions between lithium alkyls and halides of titanium and cobalt, as well as the use of these systems for initiating polymerization, was the subject of a report by N. I. Nikolayev (with B. A. Dolgoplosk, V. A. Kropachev and V. N. Zgonik – Institute of High-Molecular Compounds, Leningrad). It was found possible to form isotactic and atactic polymers by polymerizing propylene, α-butene, *iso*propyl ethylene and α-heptene under the influence of lithium alkyls and titanium tetrachloride. K. V. Nel'son (with B. A. Dolgoplosk and Ye. N. Kropacheva – Institute of High-Molecular Compounds, Leningrad) submitted data demonstrating that in natural rubber, isomerization of the *cis*-links of the polymer chain into *trans*-links takes place under the influence of titanium tetrachloride. M. I. Mosevitskii (with S. E. Bresler, I. Ia. Poddubnyi and N. N. Chesnokova – All-Union Scientific Research Institute of Synthetic Rubber, Institute of High-Molecular Compounds, Leningrad) reported on the results of investigations into the mechanism of the polymerization of isoprene in solution under the influence of catalytic masses, formed as a result of reactions between titanium tetrachloride and tri*iso*butyl aluminium. On the basis of an analysis of molecular weight distributions obtained with the aid of an ultracentrifuge, the conclusion was drawn that several types of catalytic masses are present in the system. Iu. Ia. Gol'dfarb (Institute of Petroleum of the Academy of Sciences, U.S.S.R. Moscow) in a report on the synthesis of poly*iso*butylene with a complex organometallic catalyst, submitted data on the influence of the ratio of the catalyst components and the temperature and duration of polymerization on the molecular weight of a polymer. Ye. P. Tepenitsyna (with M. M. Farbyerov – Yaroslavl' Technological Institute) reported on a new method of determining the activity of trialkyl aluminium, which characterizes the capacity of its solutions to reduce titanium tetrachloride. In as much as this process is one of the stages in the mechanism of stereoregular polymerization, this method is of great interest.

In a short report by D. A. Kochkin (on behalf of V. N. Kotrelev, S. P. Kalinina, G. I. Kuznetsova, V. V. Borisenko and M. F. Shostakovskii – Scientific Research Institute of Plastics, Moscow) data were presented on the synthesis and study of certain monomeric and polymeric silicostannoorganic and stannoorganic compounds.

The paper by O. Ia. Fedotova, N. I. Skripchenko and I. P. Loseva (Moscow Chemico-technological Institute i/n D. I. Mendeleyev) described an unpublished application for the synthesis of polyureas of the aromatic diamines—primary and alkylated with a nitrogen atom, and in the ring. The polymers obtained as a result of the reaction between such diamines and aliphatic and aromatic di*iso*cyanates were thoroughly studied, and it was established that they can be used as plastics and elastomers possessing good dielectric properties, strong adhesion to glass and metals, high tensile strength and other valuable technical properties.

Three papers were devoted to fibre-forming polymers. In the paper by G. I. Kudriavtsev, Ye. A. Vasil'eva-Sokolova and M. A. Zharkova (All-Union Scientific Research Institute of Artificial Fibre, Mytishchi) results were submitted of an investigation of the chemical transformation processes of copolymers of acrylonitrile with vinyl caprolactam and *n*-aminostyrene, which showed the possibility of transforming copolymers into polymeric dyestuffs, or of changing them so that they become easily colourable dyestuffs. In the paper by S. N. Ushakov devoted to the problems of spatial crosslinking of copolymers of vinyl acetates and vinyl alcohol with the aid of croton amide and methylol croton amide, amphasis was laid on the value of these questions for obtaining new types of very strong synthetic fibres and a number of other valuable technical materials. In the paper by Li Si-Zhi (Korean Peoples

Democratic Republic) data were submitted on the study and production of vinylon fibre. Iu. I. Zobnin (with I. S. Izmailova and O. A. Kolmakov) reported on the successful use of new dispersions of frost proof polyacrylic copolymers for dressing and impregnating leather as well as for dressing sheepskins for fur coats.

A considerable part of the papers and reports was devoted to questions of the modification of polymers.

The paper by V. A. Kargin, P. V. Kozlov, N. A. Plate and I. I. Konorev (Moscow State University) on obtaining and studying the properties of graft copolymers of styrene and starch, contained the results of research into the kinetics of ozonization of starch under various conditions, and the subsequent polymerization of styrene on ozonized starch. The various copolymers of styrene and starch obtained, were characterized by their solubility and mechanical properties. Polystyrene side chains were formed by hydrolysis of starch chains, and their molecular weight was determined, proving in a number of cases to be extremely high. The formation and study of such graft polymers is of interest due to the combination of the properties of hydrophylic and hydrophobic polymers

M. S. Akutin, B. M. Kovarskaia, L. I. Golubyenkova, K. N. Vlasova, S. P. Kalinina, N. Ia. Parlashkevich and V. N. Kotrelev (Scientific Research Institute of Plastics, Moscow) reported on the formation of a large number of graft and block polymers by intense mechanical actions, ultrasonic actions and chemical methods. Data were also submitted on the properties of the copolymers obtained.

In the communication by V. I. Serenkov (with R. S. Klimanova, V. L. Karpov and Iu. M. Malinskii—Scientific Research Institute of Plastics and Physicochemical Institute, Moscow) on the formation of graft polymers under the action of gamma radiation, results were presented of research into the action of radiation on polyethylene mixed with polystyrene or styrene, and it was demonstrated that under certain conditions, materials are obtained which have improved properties.

B. L. Tsetlin (with V. V. Korshak, S. R. Rafikov and V. A. Sergeyev—Institute of Elemental Organic Compounds, Moscow) reported on the results of aftereffect with radiation polymerization of monomers of the vinyl series. This was of interest because it now becomes possible to put into practice a continuous method of radiation polymerization, by prior irradiation of the monomer with subsequent polymerization at low temperatures outside the radiation field.

Z. N. Tarasov, M. Ia. Kaplunov, N. A. Klauzen, B. A. Dogadkin and V. L. Karpov (Scientific Research Institute of the Tyre Industry, and the Physicochemical Institute, Moscow) reported on the results of their work on the vulcanization of rubbers with the aid of nuclear radiations. Radiation vulcanization processes were studied, as well as the properties of the vulcanization products obtained.

Reports were also heard from V. D. Zaitseva (with A. S. Kuz'minskii and N. N. Lezhnev—Scientific Research Institute of Rubber and Latex Articles, Moscow) on suppressing the catalytic action of polyvalent metals in rubbers; from M. G. Zaripova (with M. S. Akutin, V. I. Guseva, B. K. Karmin, L. N. Smirnova and M. A. Stal'nova—Scientific Research Institute of the Tyre Industry, and Scientific Research Institute of Plastics, Moscow) on modification of the properties of divinyl styrene rubbers by synthetic resins; from V. K. Liubeznikov (with V. G. Epshtein and D. B. Boguslovskii—Yaroslavl' Technological Institute and Yaroslavl' Tyre Works) on the peculiarities of strengthening rubber by introducing resorcin formaldehyde resins into the latex; from Iu. L. Margolina (with M. B. Genel', B. E. Kutsenok and M. N. Kulakova—Scientific Research Institute of Rubber and Latex Articles) on the properties of carboxylate divinal styrene latexes; from S. A. Subbotin (with F. S. Shenderovich and T. N. Barbarina—All-Union Scientific Research Institute of Synthetic Rubber, Leningrad) on investigations of non-colouring antioxidants of rubber, both those already known and those synthesized for the first time.

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A number of reports in other sections was devoted to certain polymerization reactions and to the rules which govern their course, which do not directly pertain to the problems of polymer chemistry, but which are nevertheless a kind of model investigation extending our knowledge in the field of polymer science. The report by E. G. Vol'pov and A. V. Liuter (Grozna Petroleum Scientific Research Institute) belonged to this category, and concerned catalytic polymerization of amylenes, hexylenes and heptylenes on a phosphoric acid catalyst—it was heard in the section for organic chemistry and technology. Polymerization conditions were set forth in the report as well as the properties of the products obtained, which were low-molecular representatives of the polymer homologous series with five to seven carbon atoms in the chain.

Also of interest was the report by A. I. Iurzhenko and R. V. Kucher (L'vov State University) on some of the peculiarities of the course taken by chain reactions in hydrocarbon emulsions stabilized by surface-active emulsifiers, which was given in the colloidal chemistry section.

A number of reports were specially devoted to the synthesis of new cellulose derivatives, to the study of the properties of cellulose and other polysaccharides, and to their use as a raw material for obtaining a variety of chemical products. One of the sessions in the section for the chemistry and technology of polymers was devoted almost entirely to this question.

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In the report by Z. A. Rogovin and V. A. Derevitskaia (Moscow Textile Institute) concerning new methods of synthesizing cellulose derivatives and polyuronic acids, fundamental data were presented on methods of synthesizing these compounds, and on the results of investigating their properties. A method has been developed of synthesizing cellulose esters with various α-and ω-amino acids; a new class of mixed cellulose esters has been obtained with acetic acid and amino acids; a number of new cellulose derivatives have been synthesized (graft cellulose esters) and a method has been developed for synthesizing new derivatives of polyuronic acids and carboxyl-containing cellulose esters. The main characteristics of these methods were given and the prospects of further development of the works mentioned in the report were designated.

N. V. Mikhailov and Z. G. Serebriakova (All-Union Scientific Research Institute of Artificial Fibres) reported on research into mutual structural transformations of the modifications of natural and regenerated cellulose. The reporters have brought about structural transitions of natural cellulose into cellulose hydrate (without dissolving the cotton fibre) and of hydrocellulose into natural cellulose, and have thus shown by various physicochemical methods the continuity of these transitions which are accomplished through a series of intermediate structures and are characterized by a varied molecular packing density. The results obtained again indicate the absence of phase differences between natural cellulose and cellulose hydrate. Data were also given on a method developed by the authors for obtaining cellulose hydrate fibres with a molecular structure and molecular packing density characteristic for natural cellulose.

B. I. Aikhodzhayev (with V. A. Kargin and Kh. U. Usmanov—Institute of Vegetable Raw Materials of the Academy of Sciences Uzbek S.S.R. Tashkent) reported on obtaining a graft copolymer of cellulose with styrene and also with acrylonitrile. The grafting was achieved by polymerization of monomers on an ozonized cotton fibre and viscose cord. The graft copolymer of cellulose and styrene possesses strong adhesion to rubber.

A number of short communications was also heard on investigations of the various chemical and physicochemical propertise of cellulose and its satellites, and of other polysaccharides and their derivatives. Among these communications were those by Ye. A. Plisko

(with S. N. Danilov—Institute of High-Molecular Compounds) on the search for new ways of synthesizing the simple esters of cellulose and chitin; by N. S. Nigmankhodzhayeva (with Kh. U. Usmanov—Institute of Vegetable Raw Materials, Tashkent) on the dependence between the mechanical and thermodynamic properties of cellulose fibres in organic fluids; by G. S. Smirnova (Moscow Textile Institute) on research into the comparative reactivity of the hydroxyl groups of the macromolecular polysaccharides (amyloses, laminarines) in esterification and alkylation reactions; by V. P. Levanova (with V. I. Sharkov—All Union Scientific Research Institute of the Hydrolysis and Sulphite Alcohol Industry) on the packing density and reactivity of cellulose; by A. S. Freidin (with Iu. M. Malinskii, V. L. Karpov and N. T. Romanov—Central Scientific Research Institute of Wood Machining, Physicochemical Institute, Moscow) on a study of the action of ionizing radiation on wood; by F. I. Sadov (with R. I. Vylcheva—Moscow Textile Institute) on the action of light on cotton fibre cellulose; by O. P. Koz'mina (with V. I. Kurliankina, Ye. N. Matveyeva and M. K. Aleksandrovich—Institute of High-Molecular Compounds) on the mechanism of oxidative decay in cellulose esters, and inhibition of the oxidation reaction; by I. N. Yermolenko (with S. S. Gusev and V. I. Ivanov—Institute of Organic Chemistry i/n N. D. Zelinskii of the Academy of Sciences, USSR, Moscow) on a spectral study of oxidized celluloses; and by L. Ye. Akim (with N. A. Rusina, V. Ye. Kil'kki and L. Ia. Zbrozhek—Leningrad Technological Institute i/n Lensovyet) on obtaining and studying refined sulphite cellulose for high-strength cord fibre.

A number of works on the study of the properties of cellulose and other polysaccharides, particularly starch, were presented at the colloidal chemistry section.

In the paper by G. V. Nemirov (Rostov on Don State University) experimental data were submitted concerning the sorption by cellulose of certain salts from their aqueous solutions. Certain conclusions can be drawn from these data about the reason why the sorption of salts by cellulose should vary. This is connected with the temperature values of ion hydration. Moreover, on the basis of these investigations ,conclusions can be drawn concerning the relationship in cellulose of free and hydrogen bonded hydroxyl groups.

V. I. Iakimova, S. L. Talmud and K. P. Mishchenko (Leningrad Technological Institute i/n Lensovyet) reported on their work on the interaction between cellulose and fluids, which is based on the determination of heat effects.

In the same section, works were heard on certain properties of starch. In the short communication by M. I. Kniaginichev and Iu. P. Boklhovitin (Leningrad Technological Institute of the Food Industry) data were presented on the properties of starch in salt solutions. The paper by O. D. Kurilenko and Ye. A. Iakovkina (Kiev Technological Institute of the Light Industry i/n A. I. Mikoian) concerned the phenomenon of contractions of systems when a solid component is wetted by fluids. This phenomenon was studied in starch, and it was shown that data on the contraction of similar systems, show the same characteristic of interaction between water and polymers which are similar to starch, as data on the temperature of wetting.

A number of works read at various sections were devoted to lignin. In the paper by N. N. Shorygina, A. A. Chuksanova, A. F. Semechkina and L. L. Sergeyeva (Institute of Organic Chemistry i/n Zelinskii of the Academy of Sciences, U.S.S.R., Moscow) on nitration of lignin and model compounds, which was read at the section for the chemistry and technology of polymers, results were given of investigations on a number of low-molecular compounds which are, apparently, structural elements of lignin. For this purpure, compounds were synthesized which are models of the final and intermediate links of lignin molecules, and a study was made of the action of nitric acid on these compounds in a carbon tetrachloride medium. The data obtained concerning nitration of model substances, made it possible to form a concept of the complicated and varied transformations of lignin when treated with nitric acid.

Interesting papers on the ways in which lignin forms in a living plant (V. N. Sergeyev, Z. N. Krieitsbyerg and L. N. Mozheiko—Institute of Forestry Problems of the Academy of Sciences, Latvian S.S.R, Riga), and on lignin in fossilized and new wood (S. M. Manskaia and L. A. Kodin—Institute of Geochemistry and Analytical Chemistry i/n V. N. Vyernadskii of the Academy of Sciences, U.S.S.R, Moscow) were heard at the section for the chemistry of natural compounds and biochemistry.

In the same section, the paper by Ye. L. Rozenfel'd was heard (Laboratory of Physiological Chemistry, Academy of Sciences U.S.S.R., Moscow) which concerned research by the enzyme method into the structure of polyglucosides of the dextran type. The lecturer stated that deciphering the minute structure of grafted polyglucosides became possible only when the enzyme method began to be used for studying their structure in combination with the previous chemical methods. Thus, with the aid of ferments which catalyse the decay of final 1,4-bonds in the polysaccharide molecules, and also ferments which break down branch bonds (1,6-bonds), it was possible to establish the length of the internal and external chains in the molecules of various glycogens. The lecturer presented new experimental data in this field.

In the same section, L. I. Kurgul'tseva (Institute for the Chemistry of Vegetable Matter of the Academy of Scienses Uzbek S.S.R., Tashkent) gave an account of experimental data on the part played by sugars in the biological synthesis of cotton cellulose in the cotton plant, which show that synthesis of cellulose in the cotton plant is apparently accomplished in two ways: through phosphorus esters of sugar, and directly from the sucrose, by-passing the formation of phosphorus esters.

Finally, questions of obtaining various chemical products from vegetable raw materials was the subject of the communication by V. N. Sergeyeva (Institute of Forestry Problems, Riga) at the section for the chemistry and technology of polymers, who reported work which she has carried out with A. I. Kal'ninsh, on ways of obtaining levoglucosan from vegetable waste. It was also the subject of two communications at the organic chemistry and technology section, one of which (by A. A. Prianishnikov, P. D. Borisov, A. N. Vodzinskaia, I. A. Griporov, S. O. Skortsov, U. P. Sumarokov and I. F. Chistov – Central Scientific Research Institute of Wood Pulp Chemistry, Khimki, Moscow Oblast', and All-Union Scientific Research Institute of Chemical Reagents, Moscow) concerned extensive work on obtaining reagents and preperations from the intermediate products and waste of wood pyrolysis; the other (by M. Ye. Shpuntova, Ye. Ye. Shneider and S. V. Chepigo—All-Union Scientific Research Institute of the Hydrolysis and Sulphite Alcohol Industry, Moscow) concerned an investigation into the combined method of hydrolysing vegetable substances with concentrated sulphuric acid.

The problems concerning the dependence of the properties of polymers on the constitution of polymer chains and the structure of polymers, form a substantial section of polymer science. These dependences determine the behaviour of polymers when worked, as well as the formation of these or those physical and technical properties in both polymer materials and in articles made from them. A considerable number of papers and communications was devoted to these problems, and most of them were heard in the section for the chemistry and technology of polymers.

V. I. Selikhova, G. A. Markova and V. A. Kargin (Physico-chemical Institute, Moscow) reported on a comparative study of orientation processes in crystalline and amorphous polymers in the region of their softening point. The data obtained on the character of the molecular order of orientated polymers below and above the melting or vitrification temperatures (an orientated state ofter softening was preserved, thanks to a special prodecure) showed that marked changes in the order of the chains in the melting and softening region only take place in crystalline polymers.

In the paper by V. A. Kargin, V. A. Kabanov and I. Iu. Marchenko (Moscow State University) on the mechanical properties of isotactic polystyrene, obtained by polymerizing styrene on a catalyst of the Zeigler type, new, extensive data were submitted on the temperature dependence of the mechanical properties of this polymer, both in the amorphous and crystalline states. Moreover, a study was made of crystallization processes which develop in amorphous isotactic polystyryne, and also the connection was shown between a number of mechanical properties and the kinetics of the process of recrystalization, which develops with deformation of crystalline polystyrene. The close results obtained for the influence exerted by the kinetics of crystallization and recrystallization when deforming polyethylene terephthalate on its mechanical properties, were also reported by L. Z. Rogovina (with G. L. Slonimskii—Institute of Elemental Organic Compounds of the Academy of Sciences, U.S.S.R).

Several short reports were devoted to studying the properties of macromolecules and interaction between them.

M. B. Kostantinopol'skaia (Physico-chemical Institute Moscow) reported on an electron microscope study of the dependence of the shape of macromolecules on the surfaces of various solid catalysts; O. B. Ptitsyn (with T. M. Birshtein and Iu. A. Sharonov—Institute of High-Molecular Compounds) told about the results of theoretical research into the connection between the dimensions and dipole moments of macromolecules in solution, and the stereochemical structure of chains and the conditions of internal rotation which they contain; in the communication by L. L. Burshtein (with G. P. Mikhailov—Institute of High-Molecular Compounds) experimental data were presented, which had been obtained when investigating molecular interaction in polymers by studying their dielectric polarization, and which testify to the great new possibilities of this method; V. N. Nikitin (with B. Z. Volchek—Institute of High-Molecular Compounds) reported on research into the mechanism of tension in polyethylene, polyvinyl acetate, gutta percha and rubber from natural rubber by the method of polarizational infra-red spectra. The data submitted, confirmed the concept about the rotational isomeric mechanism of tension in polymers.

In the paper by V. Ye. Gul' (Moscow Institute of Fine Chemical Technology) entitled "The influence exerted by additional orientation in material at the point where the breaking region grows, on the mechanical destruction process of elastomers", data were presented on a study of the degree of orientation in elastomers in the region of destruction of a uniaxially extended specimen. The data were obtained by using the method of high-speed cine filming in polarized light. A study of the destruction process of various rubbers, polyethylene and polymethyl methacrylate in a wide temperature range showed differences in the behaviour of these polymers, explained by the difference in the molecular structure and physical properties.

Several papers and communications were devoted to questions of flow in polymers.

P. Piganiol and A. Kepes (of France) gave a speech on certain properties of polymer melts, in which he reported on measurements of flow in silicones, polyamides polystyrene, polyethylene and other polymers at various temperatures, carried out with the aid of a new microconsistometer which makes it possible to measure viscosities between 0·01 and 10^5 poises in a wide range of temperatures. Describing in detail the design of the instrument, which is in essence a rotational viscometer of improved design, the lecturer also explained the theory of it and the method of calculating the data obtained.

V. A. Kargin, A. S. Novikov and F. A. Galil Ogly (Scientific Research Institute of the Rubber Industry, Moscow) reported on flow at high temperatures in vulcanization products of rubber-like fluorine copolymers whose crosslinking had been produced by a variety of methods. By studying the temperature dependence of the rate of relaxation they were able to draw a number of conclusions about the mechanism of relaxation processes and about flow in various types of space-crosslinked, filled and unfilled elastic fluorine copolymers.

G. M. Bartenev, N. V. Zakharenko and F. S. Tolstukhina (Scientific Research Institute of the Rubber Industry, Moscow) reported on results of investigating flow in rubber-like polymers and raw rubber mixtures. As a result of studying the laws of flow in these materials ove ra wide range a wide range of temperatures, shearing stresses and shearing rates, empirical dependences have been established between shearing stress at a constant rate gradient and yield strength on the one hand, and between the shearing strength of a material and the plasticity according to Karrer on the other hand. A method was also suggested for comparative evaluation of technological properties of mixtures for conversion processes. B. M. Gorelik (with R. V. Torner, N. I. Kirschenshtein and M. V. Spitsyna—Scientific Research Institute of the Rubber Industry, Moscow) reported on certain peculiarities in the rheology of fluorine rubbers and rubber mixtures based on them, which were studied with the aid of a specially developed capillary viscometer; also on a new method of industrial quality control of the flow of fluorine rubber. A. S. Novikov (with F. S. Tolstukhina—Scientific Research Institute of the Rubber Industry, Moscow) reported on investigations carried out on the flow of filled mixtures of polydimethyl siloxanes with low shearing stresses, and on the comparison of these data with the properties of vulcanized rubbers. The results obtained made it possible, by measuring the change in the mechanical properties of an unvulcanized mixture, to estimate the activity of fillers and the chemicomechanical processes which develop on rolling the raw mixtures.

In the report by G. N. Buiko, N. M. Arenzon, A. I. Tumanov and N. P. Zinchenko (Scientific Research Institute of the Tyre Industry, Moscow) entitled "Basic Problems of Raising the Dynamic Endurance of Multilayer Rubber Systems", data were set forth from systematic investigations of various doubled rubbers and rubber-cord systems. The results of the laboratory investigations and also of the tyre tests ahowed the correctness of recently developed concepts about the exceptionally important part played by the fatigue characteristics of rubbers in the dynamic endurance of multilayer systems.

In the communication by Ye. Ia. Iaminskaia (with V. A. Kargin, I. P. Nadgas'eva and V. A. Berestnev—Scientific Research Institute of the Tyre Industry, Moscow) on the heat resistance of cord from polyamide fibres, it was stated that heat resistance and dynamic endurance of such cord at high temperatures depend on the content of impurities in the cord which, when they oxidize, initiate oxidation decay in the polymer itself.

G. L. Slonimskii (with Ye. V. Reztsova and G. P. Drugova—Scientific Research Institute of the Tyre Industry) reported on the part played by chemicomechanical phenomena in the processes of forming mixtures of two polymers, and he also stressed the possibility of mutually mixing spatially crosslinked polymers by employing the chemical flow process.

A. G. Shvarts (Scientific Research Institute of the Tyre Industry) briefly presented the results of his investigations into the dependence of the principal mechanical properties of rubber made from synthetic isoprene material, upon the density of the crosslinks in the vulcanization products, determined by the swelling method.

In the report by O. N. Byeliatskaia, B. A. Dogankin, M. S. Fel'dshtein and I. I. Eitingon (Scientific Research Institute of the Tyre Industry; Moscow Institute of Fine Chemical Technology) entitled "Sulphenamide Compounds As Vulcanization Accelerators", data were presented testifying to the radical character of the action of sulphenamide accelerators. Various accelerators of this type were synthesized and their action on the vulcanization process studied.

A comparative study of the various sulphenamide derevativs of mercaptobenzothiazole makes the use of these accelerators seem promising under circumstances of abridged mixing conditions of highly active fillers and vulcanization at elevated temperatures.

M. P. Zverev (with P. I. Zubov—All-Union Scientific Research Institute of Artificial Fibre, Matishchi: Physico-chemical Institute i/n Karpov, Moscow) reported on an investigation of the interaction between plasticizers and active fillers, which showed that the mo-

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duli of elasticity, the integral sweeling heat and the energies of intermolecular interaction in the system filler–plasticizer depend upon the value of the dipole moment of the plasticizer molecules.

L. V. Sergeyev (State Optical Institute i/n S. I. Vovilov, Leningrad), in a communication on the adhesion of polymers to silica glass, showed that, on a level with the chemical constitution of the polymer link and its general physico-chemical properties, a basic influence on the strength of the adhesion of a solidifying polymer to glass is exerted by the molecular weight of the polymer and by the characteristics of the solution applied to the glass.

N. S. Tihkomirova (with Iu. M. Malinskii – Physico-chemical Institute, Moscow, Scientific Research Institute of Plastics, Moscow) described an investigation into the influence of gamma radiation on the diffusion characteristics of certain polymers (polyethylene, polyamides, polytetrafluorethylene, SKS-30, polyvinyl chloride). Data were submitted on the dependence of the penetration and diffusion factors of inert gases upon the dimensions of the gas molecules, the nature of the polymer, the irradiation doses and the temperature.

S. A. Pavlova (with S. R. Rafikov and I. I. Tverdokhlebova – Institute of Elemental Organic Compounds, Moscow) gave an account of an experiment to use precision ebulliscopy for determining the molecular weight of polymers.

The paper by A. B. Pakshver (All-Union Correspondence Institute of the Textile and Light Industry, Moscow) entitled "The Molecular Structure and Properties of Chemical Fibres" was devoted to the important question of the influence exerted by the method of forming fibres and also their further treatment upon the relative position and shape of the macromolecules, and consequently upom the overall properties of the fibres as well. As a result of an investigation into the influence of heat treatment on the physico-chemical properties of caprone and polyacrylonitrile fibres, into the influence of drying on the properties of viscose fibres, it was shown that as a result of these processes a change in the character of the molecular packing takes place, which is clearly manifested in a change of density, thermodynamic properties, penetrability etc. Also demonstrated was the influence of the state of the initial fibre on the processes which develop in the with further heat treatment and machining.

L. V. Kozlov (Institute of Elemental Organic Compounds) reported on the influence exerted by the structural regularity of mixed polyamides of 2,2′-*bis*-[5(4H)-oxazolones] and diamines on the properties of such polymers. These polyamides, distinguished by a strictly defined order in the arrangement of monomer residues from mixed polymers formed from the same initial substances using polycondensation, possessed a higher melting temperature and lower solubility. In the case of regular constitition, the influence of the various structural elements of the macromolecule is also manifested more sharply.

Finally, a number of communications at the polymer section were devoted to questions of macromolecular decay.

T. G. Degteva and A. S. Kuz'minskii (Scientific Research Institute of the Rubber Industry) reported on the mechanism of thermal decay in certain fluorine polymers. By studying the volatile products evolved from fluorine-containing rubber-like polymers *in vacuo* and in oxygen at high temperatures, and comparing these data with the infra-red spectra of through-heated polymers, it was possible to draw the conclusion that, in certain cases, a system of conjugate bonds is formed in the polymer (copolymer of vinylidene fluoride and trifluorochlorethylene when heating *in vacuo*), whereas when through-heating in a medium of oxygen, conjugate bonds are not formed. It was also shown that in order to obtain heat resisting fluorine polymers it is necessary to thoroughly cleanse the initial monomers from impurities. B. L. Yerusalimskii (with B. A. Dolgoplosk, T. N. Kuren'gina and Ye. I. Tinishkova – Institute of High-Molecular Compounds) spoke about the mechanism of decomposition of polymers under the influence of the free radicals, and showed that the primary event towards decomposition of polymers in this case is the detachment of the H-atom from the

polymer chain. A. G. Popov (with S. Ye. Bresler, E. N. Kozbekov, A. G. Os'minskaia and Ye. M. Saminskii—Institute of High-Molecualr Compounds) spoke about research into the decomposition of polypropylene at elevated temperatures. A study was made of the decay products of polypropylene *in vacuo* and in the presence of oxygen, as well as of the influence of antioxidants on polypropylene decay when heating in air. It was shown that diphenylol propane leads to the inhibition of decomposition of this polymer at 150°.

A number of papers and communications directly concerning the comprechension of the properties of polymers were heard at the sessions of the colloidal chemistry section.

Great interest was aroused by the detailed report by P. A. Rebinder on the main problems of the physico-chemical mechanics of dispersed and high molecular structures. Pausing on a definition of this new branch of learning which has arisen on the boundary between colloidal chemistry, molecular physics and the mechanics of materials, the lecturer gave a detailed description of the objective of this new complex science with its specific problems; these fall into two groups—those requiring further development, and those which are still in the initial stages of growth. Problems of the rheology, mechanics and molecular physics of solids and crosslinked systems belong to the first group of problems. Belonging to the second group, are the problems of controlling both machining processes and processes for obtaining solids with prespecified properties, such as building materials, polymer materials with the use of active fillers and plasticizers, heat resisting and durable materials, and coatings of glass and metal ceramics. In the opinion of the speaker, the following divisions of polymer chemistry and technology enter within the sphere of this new branch of learning: pressure machining of space crosslinked polymers and vulcanization products using chemical decomposition and recombination of free radicals while still in the deformed state; new mechanical methods of polymerization to form ready made articles; and reprocessing latex systems. Rebinder gave a most illuminating account of the problems connected with the formation of coagulation condensation crystallization structures and defective (disperse) structures of solid surfaces.

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In the report by N. A. Krotova and A. P. Morozova (Institute of Physical Chemistry), light was thrown on questions of adhesion bonding and methods of investigating it. Experimental data on the adhesion of polymers to polymer surfaces, and of polymers to modified surfaces of glass, have made it possible to develop concepts about the electrical nature of adhesion in the case of the polar components of the system, and about the diffusion nature of adhesion in the case of the non-polar components.

Ye. M. Aleksandrova, V. N. Tsvetkov and N. S. Razumikhina (Moscow Chemicotechnological Institute) reported on the work which they have carried out in conjunction with T. I. Berezinskaia and Ye. A. Chelintseva on studying some of the questions of coagulation of polystyrene latexes without electrolytes, which is one of the essential colloidal problems of polymer chemistry. In the communication by E. V. Frisman (Scientific Research-Institute of Physics, Leningrad State University i/n A. A. Zhdanov) light was thrown on the optical properties of macromolecules of polymers in solution.

A number of works given at the sessions of the colloidal and other sections, concerned a study of the behaviour of albuminous substances and the characteristics of their properties. Thus, in work the by S. M. Levi on research into the structural and mechanical properties of gelatin and photographic emulsions, and in the work by V. A. Mul'tseva on the change in the degree of swelling and the shift of the isoelectric point of emulsion and gelatin layers under the influence of surface-active substances introduced into the photographic emulsion (both these works were carried out at the All-Union Scientific Research Cine-photo Institute, Moscow), a study was made of the behaviour and certain properties of gelatin, which is a constituent part and protective component of photographic emulsions. Both these communications were heard at a session of the colloidal chemistry section.

The dependence between thermal and ultra-violet denaturation of albumens, was the subject of a communication by A. G. Posynskii (Institute of Biochemistry i/n A. N. Bakh of the Academy of Sciences, U.S.S.R., Moscow) given at a session of the section for the chemistry of natural compounds and biochemistry. He has theoretically deduced a formula, quantitatively connecting the quantum yield when denaturing albumens using ultra-violet rays with the heat of activation from thermal denaturation, which is valid for the entire range of molecular weights of albumens, from insulin (mol. wt. 12000) to the virus of tobacco mosaic (mol. wt. 42×10^6).

L. A. Bliumenfel'd (Institute of Chemical Physics, Moscow) reported at a session of the physical chemistry section on experimental data concerning the spectra of electronic paramagnetic resonance in native and denaturated albumens compared with amino acids and elementary peptides when irradiated by γ-rays. On the basis of these and other data, certain concepts were formed of the mechanism of the processes of migration and transformation of energy in biological objects.

The report by S. Ia. Frenkel' and S. Ye. Bresler (Institute of High-Molecular Compounds) at the same section, was devoted to the question of the change in conformation of albumens in dioxane–water mixtures and other mixed solvents. Finally in this section, the report by M. V. Vol'kenshtein (Institute of High-Molecualar Compounds) was heard with great interest. It concerned internal rotation and rotational isomerism in small and large molecules. As the speaker remarked, internal rotation determines the basic specific properties of polymer chains. The concept of rotational isomerism in polymer chains makes it possible, not only substantially to simplify calculations of their basic characteristics—geometrical, electrical and optical, but also to establish the main features of the physical mechanism of tension and melting in polymers On the basis of these concepts, the characteristics of the constitution of the chains of albumens and nucleic acids were submitted, as well as of the structure of crystalline polymers; an interpretation of the melting mechanism of polymer crystals was also presented.

Generally speaking, great attention was given at the congress to questions of the constitution and properties of natural albumens, nucleic acids, ferments, viruses and other biological objects. However, the study of these questions, which were heard for the most part at sessions of the section for natural compounds and biochemistry, was of a specific biochemical nature and is not therefore reviewed here.

The congress paid great attention to problems of economics, planning and organization of chemical production, and particularly of production in the polymer industry. At a special section of the Mendeleyev Congress, devoted to the discussion of the problems mentioned above, a wide range of questions was touched upon.

In the paper by N. N. Nekrasov entitled "Economic Problems of the Chemical Industry in the Seven Year Plan, and the Problems of the Science of Economics" (Council for Studying Productive Forces of the Academy of Sciences, U.S.S.R., Moscow) stress was laid on the economic rôle of chemical production, which is especially big at the present time, when the Seven Year Plan for the development of the national economy of the country is being fulfilled. Large scale production of synthetic materials is radically changing the structure of some branches of chemical production and is infinitely enlarging the connection between the chemical industry and the national economy. At the same time, the accelerated development of the chemical industry is determined by the precipitate growth of the whole economics of the country by the necessity to solve the main economic task of the U.S.S.R., in the shortest possible time. Emerging from this part which the chemical industry must play

in the development of the national economy of the country, the basic problems and tasks confronting the science of ekonomics in this particular field were formulated in the report.

In the reports by G. F. Borisovich and P. Kh. Khokhriakov (Physico-chemical Institute), P. A. Borisov and A. L. Rabkin (Institute of Petroleum of the Academy of Sciences, U.S.S.R., Moscow), A. I. Ravdel' (Moscow), N. A. Zeligman (Khar'kov Polytechnic Institute i/n V. I. Lenin), N. P. Fedorenko and Ye. P. Shchukin (Scientific Research Institute of Synthetic Spirits and Organic Products, Moscow; Moscow Institute of Fine Chemical Technology) and finally in the report by N. A. Trutnev, P. A. Khokhriakov and K. G. Dobrynin (Physico-chemical Institute) a wide range of questions was touched upon, concerning the development of the raw material base of the polymer industry (the raw material base as a whole, petroleum raw material, natural gases, benzene and synthetic ethyl alcohol).

N. P. Fedorenko and G. F. Borisovich (Moscow Institute of Fine Chemical Technology; Physico-chemical Institute, Moscow) illuminated the technological and economic shifts in the synthetic rubber industry. Their report gave details of questions concerning the rate of development of rubber production in the Five Year and Seven Year Plans, described changes in the assortment of rubber and gave data on the increase in the assortment available, showed changes in the structure of the raw material base of the rubber industry and presented technical and economic production indices for various types of rubber.

A report on the outlook for developing the production of chemical fibres in the U.S.S.R. was made by G. Ye. Birger and Ye. P. Ivanova (All-Union Scientific Research Institute of Artificial Fibre). It contained a short historical review of the development of chemical fibre production and the main trends of this production in the Seven Year Plan for the development of the national economy of the U.S.S.R. In this plan, viscose fibres retain the principal place, production of acetate silk will be greatly developed and finally, the most significant increase foreseen for the field of synthetic fibre production: polyamide, polyacrylic and polyester fibres. Thus for example if viscose fibres (including cuprammonium) silk) amounted in 1956 to 90·6 per cent of the total amount of chemical fibres produced in the U.S.S.R., then in 1965 these fibres will amount to 65 per cent of the total. Acetate fibre will amount to 9 per cent instead of 1·5 per cent, and synthetic fibres will amount to 26 per cent in 1965 as compared with 7·9 per cent in 1956.

A number of reports were devoted to the economics, organization of production, and to certain qualitative, technological and economic indices of automobile-tyre and tyre-cord production. Namely – the reports by A. D. Shakh Moscow Institute of Fine Chemical Technology) on some problems of cutting costs in the production and operation of automobile tyres; by B. A. Kanat'ev, L. A. Kuvaldin, M. A. Poliak and V. G. Epshtein (Yaroslavl' Technological Institute; Yaroslavl' Tyre Works; Yaroslavl' branch of the Institute "Reziноprockt" (Rubber Projecting) on intensification and creation of continuity in the production of automobile tyres; by F. I. Iashunskaia and A. G. Gur'evich (Scientific Research Institute of the Tyre Industry) on the technical and economic effect of increasing the quality of tyre cord; by F. I. Iashunskaia (Scientific Research Institute of the Tyre Industry) on the running cost and quality of tyres; by S. P. Potamoshnev (Scientific Research Institute of the Tyre Industry) on the reserves for increasing operating efficiency in the tyre industry; and finally the report by Ye. S. Gorovich (Scientific Research Institute of the Tyre Industry) on the economic characteristics of the rubber industry in the U.S.A. Two special reports were devoted to questions of the application of polymers: one – application in building (I. V. Rastanin – Gosstroi (State Construction), attached to the Council of Ministers, U.S.S.R., Moscow), the other – application in light industry (L. I. Itin – Moscow State Institute of Economics).

In spite of the youth of polymer science, which was formed into an independent branch of learning at the end of the 1920's, its origins were laid down much earlier. Therefore the development of some of the questions connected with the history of the birch and development of polymer science and its applications was of distinct interest. In this respect the following communications were heard with great attention at the section for the history of chemistry and chemical technology: by T. A. Favorskaia (Leningrad State University) on the formation and development of the A. E. Favorskii School; by A. Ia. Averbukh and T. S. Kudriavtsev (D. I. Mendeleyev Archives Museum attached to Leningrad State University) on the notebooks on pyrocollodion used by D. I. Mendeleyev; and the report by A. A. Berlin and S. R. Rafikov (Laboratory of Anisotropic Structures of the Academy of Sciences, U.S.S.R., Moscow; Institute of Elemental Organic Compounds) on the main stages in the development of the chemistry of high-molecular compounds. It is well known that in 1875 A. M. Butlerov first discovered the reaction of polymerization, i.e. the synthesis of polymers from low-molecule compounds (monomers). In an attempt to expand the field of study of the polymerization processes of ethylene hydrocrabons, A. M. Butlerov suggested that his pupil, the student A. E. Favorskii, study the polymerization of cromonylene. And so from Butlerov, through A. E. Favorskii to S. V. Lebyedev—Favorskii's pupil—the creator of the Soviet synthetic rubber industry, and further to the wide circle of Soviet researches of polymer synthesis, the historical footpath was extended to one of the main highways in the development of polymer science in the U.S.S.R. It was precisely this part of the communication by T. A. Favorskaia which is of undoubted interest for the history of the development of polymer science in the U.S.S.R.

The communication by A. Ia. Averbukh and T. S. Kudriavtseva is of great value, in that it gives an indisputable right to claim the priority of Russian science in solving the main scientific and technical problems of gun powder production, which is one of the applications of polymer science.

The reports and communications heard in the field of polymer science at the sessions of a number of sections, and primarily at the sessions of the specially-organized section for the chemistry and technology of polymers, were a subject of lively discussion and demonstrated the vast successes in the development of this science over recent years in our country. In the same way the VIII Mendeleyev Congress on general and applied chemistry summed up the state of scientific-research and technological works in the main sections of chemical science, including the field of high-molecualr compounds, both in respect of the synthesis of new polymers and the development of the general theory of polymer chemistry, and in respect of solving a variety of technological, technical and economic problems confronting the polymer industry.

At the same time, the summary showed that some sections of Soviet polymer science are lagging behind. Without stopping on individual particularized questions, we should like to remark on the absence of reports and communications on the largest and most important sections of polymer chemistry, which showed insufficient attention paid to these sections both by the planning organizations and by the research establishments themselves. Thus for example, absolutely no results were presented at the congress, of work in the field of synthesis and proporties of inorganic polymers, although it is well known that this field of polymer chemistry is of great importance for solving the current problem of obtaining super heat resisting rubbers and plastics. Absolutely no results were presented at the congress of work on processes and equipment for converting fused polymers into polymer materials and articles, on designing equipment and setting up scientific bases for such designing, with the object of converting fused polymers to polymers, and also with the object of forming some new types of polymer (for example graft polymers) by chemico-mechanical methods, which is one of the tasks of the Soviet equipment-building industry. The absence of reports and communications in this field at the Mendeleyev Congress, where a special

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section had been organized for processes and equipment, shows that in this section as well, work has not been developed to a sufficient level. Bringing these and other backward sections of the polymer-science front on a level with the other sections, as well as further developing the whole of Soviet polymer science, are the main tasks which confront all chemists working in the fascinating field of polymer science in order to make the decisions of the XXI Extra-ordinary Congress of the C.P.S.U. a realiyt.

Translated by J. J. CORNISH

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SOME INVESTIGATIONS IN THE FIELD OF ETHYLENE POLYMERIZATION IN THE PRESENCE OF COMPLEX ORGANO-METALLIC CATALYSTS*

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(*Received 2 January* 1959)

Papers in the olefin and diolefin polymerization field have recently acquired very great importance. A considerable proportion of them are devoted to polymerization in the presence of catalysts based on trialkyl aluminium and titanium tetrachloride [1] originally proposed by Ziegler for the polymerization of ethylene at normal pressure.

Natta [2] succeeded in obtaining a number of polymers of α-olefins and diolefins which had remarkable regularity of structure, including a regular spatial disposition—"stereo-regularity"—by means of modified Ziegler catalysts (using solid titanium trichloride). Natta termed such structures "isotactic" and "syndiotactic" as distinct from the non-regular "atactic" structures. Such stereo-regularity endows these polymers with a high degree of crystallinity and high mechanical properties which are connected with the former.

In a number of papers light has been thrown on the properties of various stereo-regular polymers of olefins [3,4] and diolefins [5,6] obtained with the aid of catalysts of the above type.

ON THE NATURE OF THE CATALYST COMPLEX

In the literature much attention is devoted to the description of the properties of stereo-regular polymers and to possible polymerization mechanism. Very little is known of the nature of the catalyst itself; at the same time more precise information on this question would allow one to control the polymerization process and to get closer to an understanding of its mechanism. We have studied the triethyl aluminium-titanium tetrachloride system. Triethylaluminium reduces titanium tetrachloride by the reaction

$$Al(C_2H_5)_3 + TiCl_4 \rightarrow TiCl_3 + Al(C_2H_5)_2Cl + C_2H_5. \quad (1)$$

Reactions of this kind are known for magnesium organic compounds [11]. The reaction proceeds immediately upon mixing the reagents and is character-

* Vysokomol. soedin. **1**: No. 8. 1148–1158, 1959.

ized by the separation of a precipitate or a change in the colour of the solution. The colour, consistency and composition of the precipitate depend on the molar ratio (MR) of the components.

Our experiments show that the degree of reduction of the tetravalent titanium depends on the MR, temperature and duration of reaction. For MR = 1, room temperature (20°C) and short duration, the reaction proceeds according to equation (1). In this case reduction proceeds only as far as trivalent titanium. On raising the temperature we observed a further reduction of titanium to the divalent state. The diethylaluminium chloride in the liquid, phase is determined from the ratio of aluminium and chlorine (Al:Cl = 0·76) and the titanium trichloride in the precipitate is determined from the ratio Ti:Cl = 0·49 (Table 1).

TABLE 1. THE COMPOSITION OF THE CATALYST SYSTEM FOR VARIOUS MOLECULAR RATIOS $Al(C_2H_5)_3 : TiCl_4$ AT 20°C

	Taken				Composition of the reaction products								
	$Al(C_2H_5)_3$		$TiCl_4$		Liquid phase				Precipitate				
MR	Al_{ov}	Al_{act}	Ti	Cl	Al	Ti	Cl	Al:Cl	Weight for analysis	Al	Ti	Cl	Ti:Cl
	g	g	g	g	g	g	g		g	g	g	g	
1	0·0320	0·0222	0·0394	0·1165	0·0366	–	0·0308	0·72	–	–	0·0378	0·0770	0·49
1	0·0270	0·0190	0·0339	0·1009	0·0265	–	0·0284	0·67	0·1330	–	0·0290	0·0585	0·49
2	0·0594	0·0380	0·0339	0·1009	0·0625	–	0·0500	0·76	0·0982	–	0·0270	0·0318	0·85
2	0·0620	0·0380	0·0339	0·1009	0·0575	–	0·0497	0·76	0·0968	–	0·0246	0·0302	0·815
0·5	0·0270	0·0162	0·0576	0·1700	0·0252	–	0·0305	0·53	0·1933	–	0·0557	0·1122	0·49
0·5	0·0270	0·0162	0·0576	0·1700	0·0286	-	0·0290	0·56	0·2103	–	0·0572	0·1330	0·43

Note. The Ti : Cl ratio in $TiCl_4$ = 0·338, in $TiCl_3$ = 0·45, in $TiCl_2$ = 0·675. Mixing time before filtering = 15 min, experiment time up to washing = 2 to 3 hr; Al : Cl ratio in the liquid phase was calculated from Al_{act}.

The difference in the weight of the precipitate and of the sum of Ti + Cl determined by analysis, which amounts to 12 to 35 per cent for various MR's, compels one to suppose that the precipitate consists of organic titanium compounds:

$$Al(C_2H_5)_3TiCl_4 \rightarrow Al(C_2H_5)_2Cl + TiCl_3(C_2H_5). \quad (2)$$

In these compounds the titanium is determined as Ti^{3+} in analysis.

One can imagine further reduction on raising the temperature in the following manner:

$$Al(C_2H_5)_2Cl + TiCl_3(C_2H_5) \rightarrow Al(C_2H_5)Cl_2 + Ti(C_2H_5)_2Cl_2. \quad (3)$$

i.e. the diethylaluminium chloride obtained by reaction (2) plays the role of a reducing agent. For MR < 1, i.e. for excess titanium tetrachloride, reduction to Ti^{3+} proceeds in strict equality to the amount of triethylaluminium introduced if the reaction is carried out for 1–3 min at 20°C. Thus if MR = 0·5, then in the

conditions quoted above exactly 50 per cent of the titianium tetrachloride (Fig. 1a) is reduced. This reaction corresponds to equation (2). For longer reaction times an additional quantity of titanium tetrachloride is reduced on account of the reduction of the diethylaluminium chloride obtained in reaction (2):

$$Al(C_2H_5)_2Cl + TiCl_4 \rightarrow Al(C_2H_5)Cl_2 + TiCl_3(C_2H_5). \quad (4)$$

For MR = 0·5 and large reaction duration the Al:Cl ratio in the liquid phase has a value which is half way between the value for triethylaluminium chloride (0·76) and for ethylaluminium dichloride (0·38), i.e. in the liquid phase there is a mixture of these two compounds.

Reaction (4) proceeds considerably more slowly than (2), as is confirmed by special experiments performed on aluminium alkyl halides. For MR = 1 and 20°C diethylaluminium chloride, as can be seen from Fig. 1b, reduces in all only 17 per cent of the titanium tetrachloride in 15 min, while in these conditions triethylaluminium reduces the titanium completely to the trivalent state. Ethylaluminium dichloride has practically no reducing power: in all about 5 per cent of the titanium tetrachloride is reduced in 60 min with MR = 10. Ethylaluminium sesquichloride (i.e. an equimolecular mixture of diethylaluminium chloride and ethylaluminium dichloride which is obtained in the first stage of the synthesis of triethylaluminium from aluminium and ethyl chloride) exhibits reducing properties which are proportional to its content of diethylaluminium chloride.

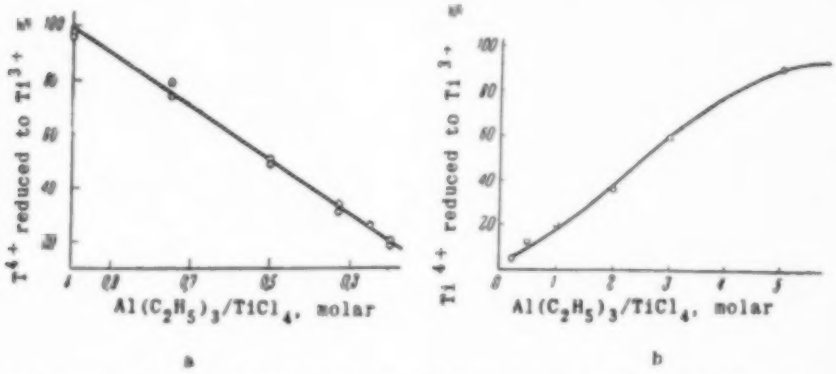


FIG. 1. The reduction of $TiCl_4$. (a) By triethylaluminium (at 20°C, reaction duration, 3 min) (b) By diethylaluminium chloride (at 20°C, reaction duration, 15 min).

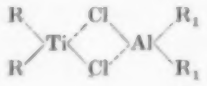
For MR > 1, i.e. with excess triethylaluminium, reduction proceeds further than the trivalent state. In this case the reaction

$$Al(C_2H_5)_3 + TiCl_3 \rightarrow Al(C_2H_5)_2Cl + TiCl_2(C_2H_5). \quad (5)$$

takes place.

In the precipitate the Ti:Cl ratio is larger than in $TiCl_3$ and even than in $TiCl_2$ (Table 1), which confirms the supposition concerning the deeper nature of the reduction of titanium. In the liquid phase $Al(C_2H_5)_2Cl$ is found.

In the case of the interaction of *bis*-(*cyclo*pentadienyl) titanium dichloride with $Al(C_2H_5)_3$. Natta [12] obtained a blue crystalline substance of the composition $(C_2H_5)_2TiCl_2Al(C_2H_5)_2$. This substance also produces polymerization of ethylene, although it is slower than when an $Al(C_2H_5)_3+TiCl_4$ mixture is used. Natta attributes the following structure to the above substance:



The formation of such stable complexes was not observed by us. All the quantities of aluminium introduced into the reaction in the $Al(C_2H_5)_3$ solution was found by us in the liquid phase (Table 1); in the precipitate aluminium was not found after carefully washing it on a filter with *iso*-octane.

It has been established unambiguously by experiments repeatedly performed by us that neither the precipitate obtained nor the liquid phase in themselves produce polymerization of ethylene separately. However, the addition of triethylaluminium to the precipitate and of titanium tetrachloride to the liquid phase makes them active again. Ziegler also points out this same feature. One can thus assume with sufficient certainty that the catalysts are unstable surface complexes which are obtained in the case of the interaction of titanium alkyl halides with trialkyl aluminium.

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THE ACTIVITY OF TRIETHYLALUMINIUM IN STEREO-REGULAR POLYMERIZATION REACTIONS AND ITS ESTIMATION

In works in the field of polymerization in the presence of metalorganic complex catalysts (of the Ziegler type) one should bear in mind the considerable lack of reproducibility of experiments which is explained by the instability of solutions of triethylaluminium and the decrease in their activity with time. The decrease in activity is connected with the great sensitivity of triethylaluminium towards the oxygen of the air with which it forms ethoxy-compounds: $Al(C_2H_5)_2(OC_2H_5)$, $Al(C_2H_5)(OC_2H_5)_2$ and $Al(OC_2H_5)_3$ [14]. Our experiments showed that the replacement of even one ethyl-group by an ethoxy-group gives a substance quite incapable of reducing titanium tetrachloride. Since the catalytic ability of triethylaluminium is directly connected with its reducing capacity in relation to compounds of tetravalent titanium, the decrease in its activity on contact with air becomes understandable. The control of the activity of preparations of triethylaluminium is thus very important for experiments on polymerization.

The methods of analysing triethylaluminium proposed by Ziegler [15] (the estimation of the aluminium and the ethyl-groups) give no idea of the change in its activity since the formation of a certain quantity of ethoxy-compounds is little reflected in the analysis results. Bonitz proposed a method of deter-

mining the activity based on the capacity of triethylaluminium to form complexses with electron-donor compounds. Complexes of triethylaluminium with isoquinoline or quinoline in the presence of diethylaluminium hydride (as a unique indicator) give colour changes analogous to the changes in acidimetry. Ethoxy-compounds do not give such complexes.

At the beginning of our work we made use of the Bonitz method to determine the activity of triethylaluminium, but it requires the special preparation of the indicator—triethylaluminium hydride which is quite difficult to achieve in the laboratory; the main defect of this method, however, is the indistinct changes in titration. Therefore, when we had established that for short reaction duration and $MR < 1$ triethylaluminium reduces a strictly equivalent quantity of tetravalent titanium (Fig. 1), we developed a technique for determining the activity from the reduced titanium [16]. The method consists in determining the quantity of titanium reduced by a known volume of triethylaluminium in 3 min. The reduced trivalent titanium is treated with iron alum and the divalent iron formed is titrated with permanganate:

$$Ti^{3+} + Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+}$$

The new method of determining the activity and the Bonitz method give comparable results (Table 2).

TABLE 2. A COMPARISON OF THE METHODS FOR DETERMINING THE ACTIVITY OF TRIETHYLALUMINIUM

$Al_{overall}$ from trilon B, (g)	By the Bonitz method		From the reduction of $TiCl_4$		$A_1 - A_2$ (%)
	Al_{act} (g)	Activity A_1 (%)	Al_{act} (g)	Activity A_2 (%)	
0·0403	0·0381	94·5	0·0378	94·0	+0·5
0·0490	0·0380	77·5	0·0380	77·5	0·0
0·0490	0·0100	22·0	0·0131	26·8	−4·8
0·0284	0·0090	31·7	0·0082	29·1	+2·6
0·0506	0·0336	66·2	0·0330	65·0	+1·2
0·0506	0·0190	37·6	0·0200	39·5	−1·9

The method proposed by us, however, has important advantages, viz. it does not require the special preparation of the difficultly accessible diethylaluminium hydride, gives distinct changes in titration and characterizes solutions of triethylaluminium by their capacity to reduce compounds of tetravalent titanium, i.e. by a property which is regarded as the first stage of the reaction in the presence of metallo-organic complex catalysts of this type.

THE INFLUENCE OF CERTAIN FACTORS ON THE MOLECULAR WEIGHT AND THE YIELD OF POLYETHYLENE

The study of the catalytic complex and the existence of a simple and convenient technique for checking the activity of triethyl aluminium, permitted us to work with a definite catalyst system and to obtain sufficiently repro-

ducible experiments on the polymerization of ethylene. Repeated attempts to perform kinetic experiments proved unsuccessful—in all cases the rate of polymerization turned out to be so great that there was no guarantee of the process proceeding in the kinetic region (especially at the beginning of the process) and it was more probable that the reaction proceeded in the diffusion region. The experiments on the elucidation of the influence of various factors on the molecular weight of the polymer are more reproducible and sufficiently reliable, but the scatter of the results must also be borne in mind in this case.

The molecular weight of the polymer, expressed in terms of the characteristic viscosity, depends on the concentration of trivalent titanium (in g/l.) in the system at the same MR = 1 and increases with increase in this concentration (Fig. 2a).

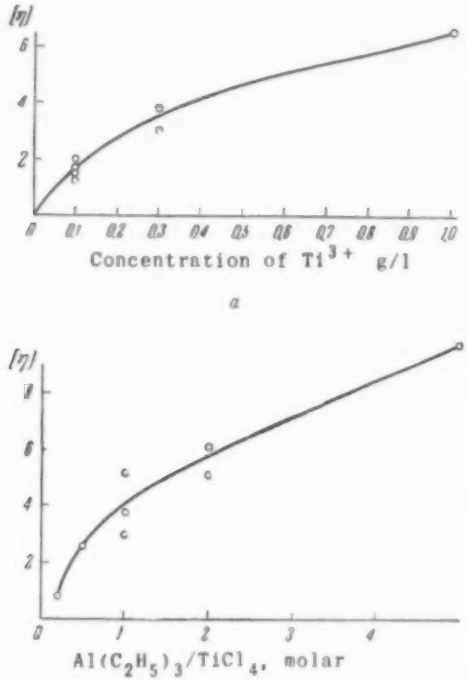

FIG. 2. The dependence of the characteristic viscosity of polyethylene. (a) On the concentration of Ti^{3+} (MR = 1). (b) On the molar ratio of $Al(C_2H_5)_3 : TiCl_4$ (concentration of reduced Ti = 0·3 g/l.).

The molecular weight also depends on the molecular ratio $Al(C_2H_5) : TiCl_4$ and is considerably increased on increasing the MR at one and the same concentration of reduced titanium (Fig. 2b), i.e. the molecular weight increases with increase in the concentration of triethylaluminium. The melting point of the polymer also varies in accordance with the molecular weight (Fig. 3).

The yield of polymer (in kg/g-molecule $Al(C_2H_5)_3$) falls somewhat with increase in the MR for the same concentration of reduced titanium (Fig. 4).

An excess of titanium tetrachloride (MR < 1) leads to a substantial reduction in the molecular weight (Fig. 2b). The molecular weight varies just as consider-

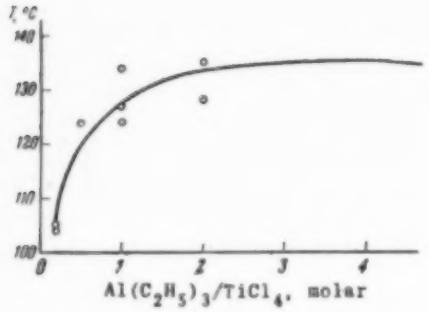

FIG. 8. The dependence of the melting point of polyethylene on the molar ratio $Al(C_2H_5)_3 : TiCl_4$ (concentration of Ti^{3+} = = 0·3 g/l.).

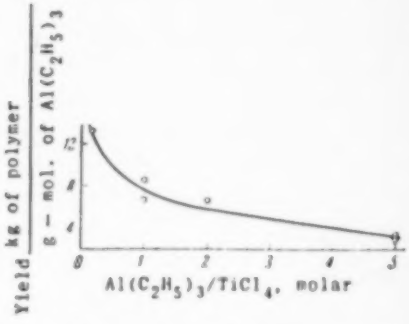

FIG. 4. The yield of polymer *versus* the molar ratio $Al(C_2H_5)_3 : TiCl_4$ (concentration of Ti^{3+} = 0·3 g/l. = const.).

ably on introducing $Al(C_2H_5)_2Cl$ into the composition of the catalyst or on replacing the $Al(C_2H_5)_3$ by ethylaluminium sesquichloride (Table 3).

TABLE 3. THE INFLUENCE OF THE INTRODUCTION OF ETHYLALUMINIUM SESQUICHLORIDE INTO THE CATALYST ON THE MOLECULAR WEIGHT OF THE POLYMER

MR	Characteristic viscosity for the system	
	$Al(C_2H_5)_3 - TiCl_4$	$Al(C_2H_5)_{1.5}Cl_{1.5} - TiCl_4$
15	—	1·62
4	9·80	1·90
2	5·10	1·70
1	4·00	1·50

Polymers which have a reduced molecular weight ($[\eta] < 1{\cdot}5$–2) are characterized by small relative elongations and brittleness.

A DISCUSSION OF THE RESULTS IN THE LIGHT OF MODERN IDEAS CONCERNING THE MECHANISM OF STEREO-REGULAR POLYMERIZATION

One of the characteristic features of stereo-regular polymerization is the necessity of the presence of a solid phase, on the surface of which the process of polymerization is realized. In our case it was shown for the $Al(C_2H_5)_3 + TiCl_4$ system that this solid phase is an alkyl titanium halide of lower valency which is insoluble in hydrocarbons and which is formed on the interaction of the two components of the catalyst.

The solid phase is capable of adsorbing the alkyls or hydrides of certain metals with small ionic radius (Al, Zn, Be, Li) [17], forming unstable surface complexes with them. In these complexes the metal alkyls and metal hydrides are in a polarized state with a displacement of the electrons in the direction of the formation of carbanions or hydride ions, which is also the primary act in the chain process in anionic polymerization [18]. Such surface complexes direct the molecules of the monomer into a definite position. The reaction proceeds as a result of the inclusion of the monomer between the catalyst complex and the growing chain. On approaching polarized $Me^+ : \bar{C}$ bond the molecule of the monomer itself polymerizes, acquiring an ability to enter into the macromolecule (6). While the growth of the chain proceeds, the polymer molecule remains attached at one end to the surface complex and grows "like a hair from a root" [18]. The reaction thus takes place in an adsorption layer where a high concentration of the molecules and their transition to an activated state are guaranteed. The possibility of polymerization in very mild conditions—at low pressures and temperatures—is explained by this fact. Ethylene polymerizes in these conditions at a high rate at normal pressure and room temperature, whereas oxygen-initiated polymerization of ethylene is carried out at 180–200°C and a pressure of ~1500 atmospheres.

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$$> \overset{+}{Me}\ \overset{-}{CH_2}-\overset{+}{CH_2}\overset{-}{CH_2} - CH_2(CH_2CH_2)_nCH_2CH_3 \qquad (6)$$

$$> \overset{+}{Me}\ \overset{-}{CH_2} - CH_2(CH_2CH_2)_nCH_2CH_3 \rightarrow > MeH + CH_2{=}CH(CH_2CH_2)_nCH_2CH_3 \qquad (7)$$

$$> \overset{+}{Me}\ \overset{-}{CH_2}CH_2(CH_2CH_2)_nCH_2CH_3 + CH_2{=}CH_2 \rightarrow > MeC_2H_5 + CH_2{=}CH(CH_2CH_2)_nCH_2CH_3 \qquad (8)$$

A break in the chain comes about in a spontaneous disproportionation of the molecule of the polymer (7) or in the transfer of the chain by the monomer (8); the metal hydride or metal alkyl is at the same time regenerated, beginning a new chain of polymerization.

The increase in the molecular weight with increase in the concentration of trivalent titanium for constant MR = 1 (Fig. 2a) observed by us can be explained by starting from general ideas concerning the factors influencing the molecular weight of polymers in the conditions of stereo-regular polymerization. They are defined by the equation [19]:

$$\bar{P}_p = \frac{k_r m_a}{k_{ts} + k_{tm} m_a + k_{ti} \cdot i}$$

where $\bar{P}_p$ is the average degree of polymerization, k_r is the reaction velocity constant for the chain growth reaction, m_a is the concentration of adsorbed monomer, k_{ts} is the reaction velocity constant for the spontaneous chain transfer by the monomer, k_{ti} is the reaction velocity constant for the stopping of the chain by impurities and i is the concentration of impurities.

With increase in the overall surface area of the solid phase (i.e. with increase in the quantity of Ti^{3+} in the system) capable of adsorbing the monomer, the

concentration m_a in the system increases. At the same time one may expect that the value of the numerator in the equation will increase to a larger extent than the denominator and $\bar{P}_p$ will increase.

In our experiments the molecular weight of the polymer increased markedly on increasing the MR for the same concentration of Ti^{3+}, i.e. on increasing the concentration of $Al(C_2H_5)_3$ (Fig. 3b). Our investigation of catalyst complexes showed that on increasing the MR a greater degree of reduction of the titanium takes place which cannot but reflect itself in the nature of the surface. It is possible that in this case its adsorption capacity increases which is due to the increase in the concentration of adsorbed monomer m_a and the increase in $\bar{P}_p$. In addition, excess $Al(C_2H_5)_3$ promotes a more complete bonding of impurities (oxygen, moisture, etc.) with their removal from the sphere of the reaction.

The lowering of the molecular weight on using excess $TiCl_4$ (Fig. 2b) can in our opinion be explained by the stopping of the chain by chlorine ions which proceeds according to the following scheme:

$$TiCl_4 \rightleftarrows TiCl_3^+ + Cl^-$$

$$>Me^+ - \bar{C}H_2CH_2CH_2CH_3 \longrightarrow + TiCl_3^+ + Cl^- \rightarrow >MeCl + TiCl_3CH_2CH_2CH_2CH_3 —$$

The stopping of the chain by chlorine ions apparently leads to a lowering of the molecular weight of the polymer in the case of a large ethylaluminium dichloride content in the catalyst:

$$Al(C_2H_5)Cl_2 \rightleftarrows Al(C_2H_5)Cl^+ + Cl^-.$$

Our data on the influence of certain factors on the molecular weight of the polymer differ somewhat from those of Natta who studied polymerization using $Al(C_2H_5)_3 + TiCl_3$ [10]. Natta observed a decrease in the molecular weight with increase in the concentration of $TiCl_3$ and he explained this by the possible blocking of the chain by impurities on the surface of the solid $TiCl_3$ introduced into the system from outside (i.e. by an increase in the value of $k_{tr} \cdot i$ in the equation for $\bar{P}_p$). In our conditions the solid phase is formed directly in the polymerization vessel itself when the $Al(C_2H_5)_3$ interacts with the $TiCl_4$, which excludes the possibility of this subsidiary influence. The solid $TiCl_3$ used by Natta is a system which differs from ours as regards surface.

EXPERIMENTAL PART

Purification of nitrogen. All the work on the investigation of the catalyst system was carried out in a nitrogen atmosphere specially purified from oxygen and dried. To remove oxygen the nitrogen was passed through a contact oven heated to 400°C and filled with a copper catalyst on silica gel [20]. The nitrogen then entered a purifying system consisting of a number of consecutive columns

containing concentrated H_2SO_4, calcium chloride, caustic soda, phosphoric anhydride, aluminium oxide and a special column filled with glass beads moistened with ethylaluminium sesquichloride.

The triethylaluminium was obtained from ethyl chloride and aluminium shavings in two stages by the Grosse and Mavity method considerably improved in our laboratory [21]. Our method makes it possible to obtain considerable quantities of triethylaluminium relatively simply.

The preparation of diethylaluminium chloride from ethylaluminium sesquichloride is based on the ability of ethylaluminium dichloride to form a solid complex on heating with sodium chloride from which diethylaluminium chloride can be distilled [22]. Diethylaluminium chloride is a colourless mobile liquid which catches fire in air; boiling point 103°C/12mm.

Percentages found: Al 22·30, Cl 29·20;
Calculated percentages for $C_4H_{10}AlCl$: Al 22·40, Cl 29·40.

Ethylaluminium dichloride was obtained by the method described by Kocheshkov and Nesmeianov [23].

Diethylaluminium hydride synthesized by a modified Ziegler method [15]. Into a flask with a mixer and a reflux condensor, was introduced a dispersion of LiH in ether to which was added an ether solution of diethylaluminium chloride; the contents of the flask were mixed for 4 hr at 30–40°C. The diethylaluminium hydride was distilled under vacuum, boiling point 97°C/10mm.

Percentage found: Al 30·3;
Percentage calculated for $C_4H_{10}Al$: Al 31·4.

The analysis of organo-aluminium compounds. The removal of samples for analysis was carried out in a stream of nitrogen with a pipette or into small ampoule for element analysis. The sample was transferred to an Erlenmeyer flask into which the solvent (*iso*-octane, petroleum ether, ether) had previously been poured and decomposed with water. Aluminium was estimated with trilon B by the method developed by the Okhtenskii chemical combine; chlorine was estimated by the Folgard method.

The ethyl groups were estimated in a Tserevitinov apparatus by the Ziegler method [15] from the quantity of gas evolved in the decomposition of the organo-aluminium compound by alcohol.

The estimation of the activity of $Al(C_2H_5)_3$ *solutions.* By the activity we mean the percentage ratio of the content of "active" aluminium, Al_{act}, i.e. the aluminium really entering into the composition of the triethylaluminium to the overall content of aluminium, $Al_{overall}$ estimated with trilon B in the triethylaluminium.

(a) *By the Bonitz method.* We used a somewhat modified Bonitz method [14]. Into the analysis test-tube, filled with nitrogen, 5 ml xylene were poured and a few drops of diethylaluminium hydride, which was titrated with quinoline to a red coloration, were added. The solution of triethyl aluminium to be analysed

was then introduced with a pipette. The colour of the liquid in the test tube changed at this point and became yellow. The colour in the test tube was again converted to red by titration with an accurately measured quantity of quinoline.

The Al_{act} was calculated from the formula

$$Al_{act} = \frac{n.c.27}{a.M} \text{ g/ml},$$

where n is the quantity of quinoline solution used in the titration, c is the concentration of quinoline (g/ml), M is the molecular weight of quinoline and a is the volume of the sample taken for analysis (ml).

(b) *By reduction of $TiCl_4$.* 50 ml of *iso*-octane were poured into a flask filled with pure dry nitrogen and the solution of triethylaluminium to be analysed and a solution of $TiCl_4$ taken in excess (Fig. 5) were introduced through a multiple side-arm.

The precipitate formed was mixed for 1–3 min and digested with water with vigorous stirring until the top layer was decolorized. The estimation of Ti^{3+} was performed by the method described by Solov'ev and Tabakova [24].

Calculation was done by the formula

$$Al_{act} = \frac{v_{KMnO_4} \cdot T_{KMnO_4}}{v_{Al(C_2H_5)_3}} \text{ g/ml},$$

where v_{KMnO_4} is the quantity of 0·1 N $KMnO_4$ used in titration, T_{KMNO_4} is the quantity of Al (in g) corresponding to 1 ml 0·1 N $KMnO_4$, $v_{Al(C_2H_5)_3}$ is the volume of triethylaluminium solution taken for analysis (ml).

The degree of reduction or the titanium was determined in the same way as the active aluminium, but the calculation was made by the technique given by Solov'ev and Tabakova [24].

The determination of the composition of the solid phase. The precipitate was filtered off on a porous glass filter No. 3, washed with *iso*-octane, dried in vacuum at 60–70°C for 4–6 hr and weighed directly on the filter. To estimate the content of titanium and chlorine the precipitate was dissolved in dilute nitric acid and the titanium estimated by means of cupferon and chlorine by the Folgard method.

The analysis of the liquid phase. To the filtrate was added water acidified with nitric acid along with the *iso*-octane wash and the *iso*-octane distilled off. The aluminium in the residual acidic aqueous solution was determined by means of trilon B and the chlorine by the Folgard method.

The polymerization of ethylene. Into the polymerization flask (Fig. 6), filled with nitrogen, was poured 150 ml *iso*-octane (before the experiment the *iso*-octane was distilled in the presence of ethylaluminium sesquichloride) and calculated quantities of $Al(C_2H_5)_3$ and $TiCl_4$ solutions were introduced through a side-arm. The catalytic precipitate obtained was stirred for 15 min at 20°C in a stream of nitrogen, after which the supply of ethylene was started. The end of polymer-

ization was determined by the cessation of the rise in temperature or from the formation of a thick unstirrable mass of polymer. The polymer was treated and washed with methanol or ethanol and dried at 80–90°C.

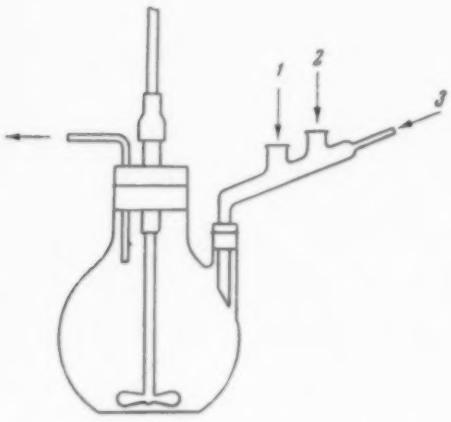

FIG. 5. The apparatus for determining the activity of triethylaluminium solutions from the titanium reduced. (1) $AlEt_3$ and $TiCl_4$ solutions, (2) *Iso*-octane, (3) Nitrogen.

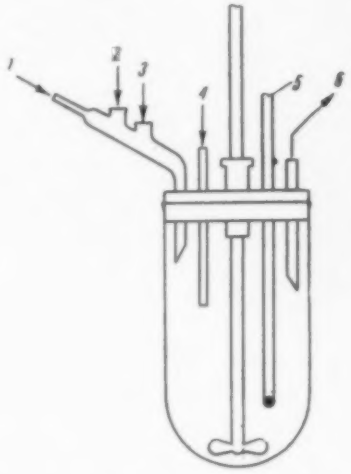

FIG. 6. Flask for the polymerization of ethylene. (1) Nitrogen, (2) *Iso*-octane, (3) $AlEt_3$ and $TiCl_4$ solutions, (4) Ethylene, (5) Thermometer, (6) Condensor.

The characteristic viscosity of the polymer was determined from the relative viscosity of solutions of three concentrations for each specimen at 110°C in xylene.

CONCLUSIONS

(1) The interaction of the components of the Ziegler catalyst system—titanium tetrachloride and triethylaluminium—has been studied. It was shown that the degree of reduction of the titanium depends on the molecular ratio of the components of the catalyst, the temperature and the duration of the reaction.

(2) The composition of the solid and liquid phases obtained in preparing the catalyst has been studied. It was shown that the stable titanium-aluminium organic complexes are absent in the solid phase. On the basis of the results obtained ideas on the nature of the catalyst complex are put forward.

(3) A method of determining the activity of triethylaluminium solutions in stereo-regular polymerization based on the ability of the latter to reduce tetravalent titanium is proposed.

(4) The dependence of the molecular weight on a number of factors has been studied.

(5) The results obtained are discussed in the light of modern concepts concerning the mechanism of stereo-regular polymerization. An attempt has been made to make these ideas more precise.

Translated by N. G. ANDERSON

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THE INFLUENCE OF LOW-MOLECULAR-WEIGHT ORGANIC COMPOUNDS ON THE ε-POLYCAPRAMIDE PHOTOCHEMICAL DESTRUCTION PROCESS*

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(*Received* 10 *March* 1959)

IN the present paper the investigation of the influence of low-molecular-weight compounds on the photochemical destruction process of polymers has been continued. The subject of the present investigation was ε-polycapramide (capron) which has received wide application in recent years.

There are few results in the literature on the photo-stability of this substance although it well-known that capron, like all polyamides, is relatively rapidly destroyed by ultra-violet radiation. It is useful to study the course of the capron photo-chemical destruction process, especially in the presence of low-molecular-weight additives investigated by us in the case of other polymers [1–3]. With this aim the compounds already described in the preceeding communications [1–3] were used. These were introduced into films of capron.

The basic method of investigation was that of studying the mechanical properties. This allowed us to establish how they change under the influence of ultra-violet irradiation. The changes in the rupture strength and deformations were determined. In individual cases the changes in the absorption spectra of the specimes in the ultra-violet region were studied.

EXPERIMENTAL PART

Specimens of industrial capron films obtained from the molten resin were used. The films were orientated in one direction. The capron used had a molecular weight from 20,000 to 23,000 (determined viscosimetrically). The thickness of the specimens amounted to 75–80 μ. The specimens were irradiated in the equipment described previously [1], in quartz apparatusses, the construction of which is shown in Fig. 1.

As low-molecular weight additives 2-oxybenz-aldazine, N-methyltoluenesulphamide, β-methyl-umbellipherone, salol and 2-(*o*-oxyphenyl)benzoxazole were

* Vysokomol. soedin. 1: No. 8. 1159 1163, 1959.

used. The absorption spectra of these compounds are given in previous communications [1,2]. The above substances were added to the already prepared films; this was achieved by keeping the specimens in solutions of the enumerated sub-

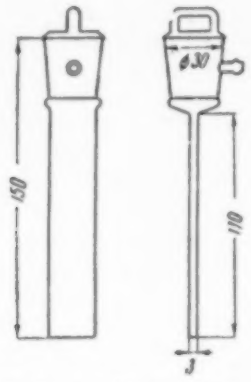

FIG. 1. The apparatus for irradiating films (dimensions in mm).

stances in ethyl alcohol in which the capron swelled. The quantities of the substances introduced into the specimens was difficult to establish, but they were undoubtedly very small. The films were dried at room temperature for a long time and were subjected to vacuum before irradiation.

For comparison specimens of capron not containing additives which had also been kept in ethyl alcohol for an equal period of time were studied. The duration of swelling amounted to several days. The irradiation of the films continued for 50 and 100 hr at 20°C, and some experiments were performed at 50°C. The changes in the mechanical properties of the specimens were established by means of a dynamometer of the Polyani type. The rupture of the specimens was carried out in the direction of their orientation. Changes in the absorption spectra in the ultraviolet range were determined by means of a spectrophotometer equipped with a rapid recording attachment.

DISCUSSION OF RESULTS

The experiments showed that in the irradiation process the properties of the capron films changed markedly.

In Fig. 2 the change in the optical properties of the specimens is shown and it is evident that with increase in the duration of irradiation the absorption of capron in the short-wave part of the spectrum also increases, which is undoubtedly due to a considerable destruction of the polymer. The specimens become yellow, this being more so on the side turned towards the source of light. The initial light-blue fluorescence of the specimens becomes stronger in the irradiation process, which is especially noticeable after 30–35 hr, the fluorescence light changing to green.

Figure 3 shows the change in the mechanical properties (strength and elongation) of the capron after irradiation. The results show a steady decrease in the rupture strength and the rupture elongation with increase in the duration of irradiation.

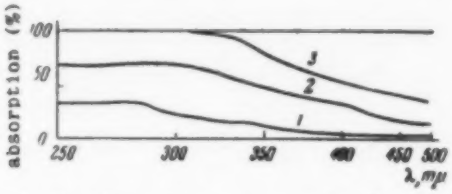

FIG. 2. The change in the absorption spectrum of a film of polycaprolactam on irradiation. (1) Before irradiation; (2) Irradiated for 50 hr; (3) Irradiated for 100 hr.

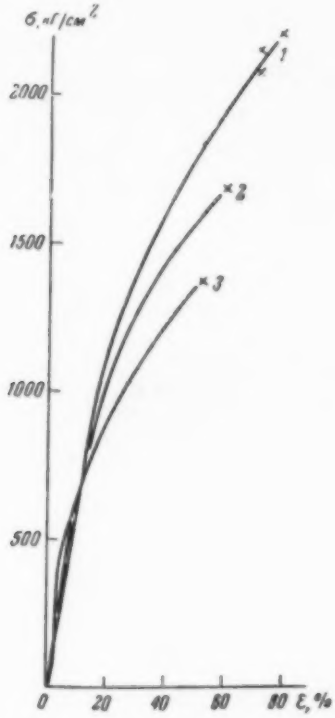

FIG. 3. The change in the mechanical properties of capron on irradiation. (1) Unirradiated capron (2); After irradiation for 50 hr; (3) After irradiation for 100 hr.

For clarity the variation of the rupture strength and rupture deformation with the irradiation time are examined seperately in Fig. 4a and b. As is evident from these Figures the decrease in the rupture strength and elongation on rup-

ture depends linearly on the irradiation time. The experimental results shows that after 100 hr of irradiation the strength and elongation decrease approximately equally and are about 60 per cent of the initial values. It is observed in addition that with increase in the duration of irradiation the elongation of the specimens obtained for the same load is also increased and one can consider that the deformation of the specimens is directly proportional to the time of irradiation. This may be explained by the fact that in the experiments the load is applied along the orientation of the film specimen and the observed phenomenon was due to a dec-

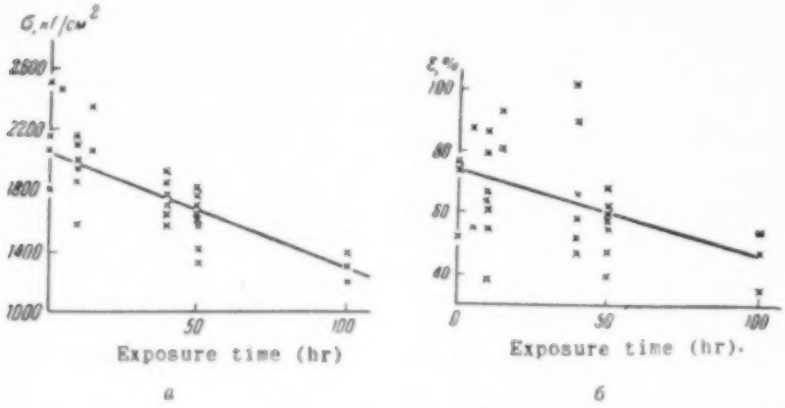

FIG. 4. The influence of the duration of irradiation: (a) Rupture strength; (b) Rupture deformation.

rease in orderliness in the specimen as a result of irradiation. It should be noted at the same time that a specimen irradiated for 100 hr and tested at small loads of up to 500–600 kg/cm² show a smaller elongation than unirradiated specimens for the same loads. Thus, in this range of loads the deformation of the specimens is inversely proportional to the time of irradiation.

This is especially noticeable in Fig. 5 where the influence of temperature on the change in mechanical properties in the process of irradiation of the capron is shown. The observed changes in the mechanical properties can apparently be explained by the appearance of a weak network structure with a simultaneous decrease in the degree of orderliness. The film will then show a great resistance to extension for small loads, but this situation will only be preserved up to a certain load limit. An increase in load above this limit has the result that the film with this structure will give a greater deformation than an unirradiated film, as was observed by us.

In Fig. 5 the change in the mechanical properties of polycaprolactam observed on irradiating specimens of it at 50°C is shown. As has already been noted earlier [3], for a solution of anide G-669 an increase in the temperature of the experiment to 50°C considerably accelerated the process of polyamide destruction. The ex-

perimental results show that after 15 hr of irradiation at 50°C capron loses its strength to the same degree as after irradiation for 100 hr at 20°C. After 15–20 hr exposure specimens irradiated at 50°C acquired a brown tinge and became less transparent.

The influence of additions of the low-molecular-weight compounds used was not exhibited wery distincly. Two of the compounds-2-oxybenzaldazine and N-mono-

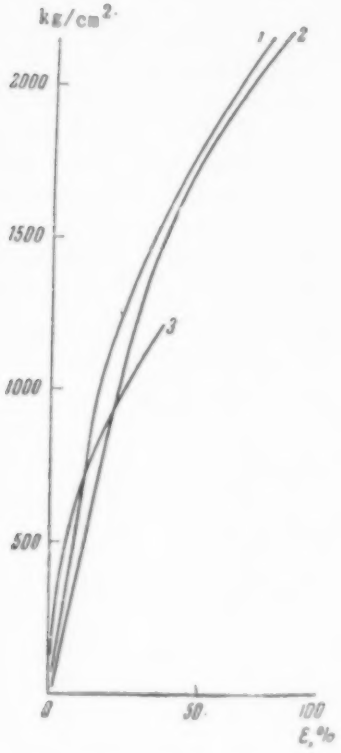

Fig. 5. The change in the mechanical properties of polycaprolactam on irradiation at various temperatures. (1) Before irradiation; (2) After 100 hr of irradiation at 20°C; (3) After 15 hr of irradiation at 50°C.

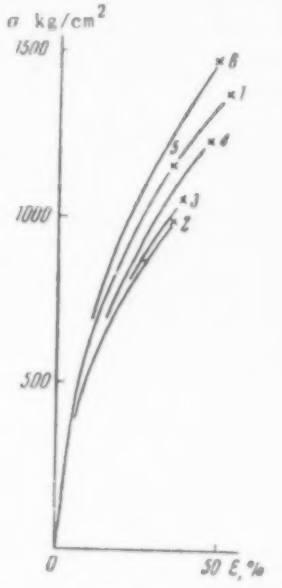

Fig. 6. The influence of low-molecular-weight additions on the change in the properties of polycaprolactam on irradiation for 100 hr. (1) Without additions; (2) Oxybenzaldazine; (3) N; methyl-toluenesulphamide; (4) β-methylumbellipherone; (5) Salol; (6) 2-(o-oxyphenyl) benzoxazole.

methyltoluenesulphamide—show an accelerating influence on the destruction process, which is known to agree with results obtained previously [3]. The loss in rupture strength and rupture elongation for a specimen with an addition of 2-oxybenzaldazine after 100 hr of irradiation is 20 per cent greater than for a specimen without an addition. The destruction of capron is accelerated in approximately the same way if N-monomethyltoluenesulphamide is added to the spec-

imen. β-Methylumbellipherone and salol showed hardly any protective action. These substances only slow down the destruction process in the first hours of irradiation. The instability of β-methylumbellipherone towards ultra-violet radiation has already been reported by us previously [1]. 2-(*o*-oxyphenyl)benzoxazole, which we used in the form of 0·005 and 0·4% solutions, had a small positive effect. Figure 6 shows the change in the mechanical properties of capron specimens with an addition of the above compounds.

Comparing the results of tests on specimens of oriented film with those on the same specimens containing additions, one may remark that substances such as 2-oxybenzaldazine and N-methyltoluenesulphamide accelerate the decrease in the rupture characteristics of the film and are sensitizers for the photochemical destruction of capron. A weak sensitizing effect is also shown by salol and β-methylumbellipherone. 2-(*o*-oxyphenyl)benzoxazole shows a somewhat better influence. At the same time it should be noted that the influence of all the additions is not very distinct and it is possible that this is due to the method of introducing the additions into the already prepared specimen of polyamide.

The authors express their gratitude to I. V. Obreimov, G. L. Slonimskii, T. A. Dikareva and L. Z. Rogovina for their assistance in the mechanical and optical testing of the specimens.

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CONCLUSIONS

(1) The existence of photochemical destruction of capron in the conditions of the experiment described is confirmed.

(2) Temperature is shown to have an accelerating influence on the photochemical destruction of capron films.

(3) It has been shown that 2-oxybenzaldazine and N-methyltoluenesulphamide are sensitizers for the photochemical destruction of capron in the conditions of the experiments.

(4) Salol, β-methylumbellipherone and 2-(*o*-oxyphenyl)benzoxazole are shown to have a weak retarding influence on the photochemical destruction process.

Translated by N. G. ANDERSON

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THE INFLUENCE OF LOW-MOLECULAR-WEIGHT COMPOUNDS ON THE PHOTOCHEMICAL DESTRUCTION OF THE POLYAMIDE ANIDE G-669*

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(*Received* 10 *March* 1959)

THE results of investigations of the photochemical destruction process in solutions of the polyamide Anide G-669 in ethyl alcohol and mixtures of the latter with dichlorethane [1] were published earlier by us. The influence of certain low-molecular-weight organic additions also used by us in studying the photochemical destruction process of other polymers [2–4] was indicated at the same time.

In the present investigation we have studied the photochemical destruction of films of the polyamide G-669. The results of the investigation permitted us to establish how the mechanical properties change in the irradiation process and thereby to supplement the experimental data obtained earlier.

EXPERIMENTAL PART

The polyamide films were prepared from 15–20% solutions of anide G-669 (molecular weight = 17,000) in ethanol. The films were dried for long time at room temperature and were exposed to vacuum before use. The thickness of the films varied from 0·002 to 0·0055 cm. Since the films were deposited from solution it was not always possible to obtain specimens of identical mechanical properties. Additions in quantities of 0·1 per cent of the weight of polymer of low-molecular-weight compounds to the solution were made before deposition of the film. In some cases in which the ability of the substance to combine with the polyamide permitted it the quantity of low-molecular-weight compound was increased to 2 per cent (2-(*o*-oxyphenyl)-benzoxazole, salol and N-methyltoluenesulphamide). The following compounds were used as additions in the present investigation: 2-(*o*-oxyphenyl)benzoxazole, salol, 1,4-diphenylbutadiene, dixanthylene, diethyl, 2,5-dioxyterephthalate, 2-oxybenzaldazine, N-methyltolurnesulphamide, *β*-methylumbellipherone, 5,7-dioxy-4-methylcumarene and 3-acetylcumarene.

The absorption spectra of the first eight compounds are shown in the preceeding communications [1–4] and those of the last two are given in the Figure and in the Table.

* Vysokomol. soedin. 1: No. 8, 1164–1169, 1959.

TABLE 1. THE INFLUENCE OF ADDITIONS OF LOW-MOLECULAR WEIGHT SUBSTANCES ON THE PHOTOCHEMICAL DESTRUCTION OF FILMS OF ANIDE G-669

Addition	Quantity added (%)	Irradiation time (hr)	Residual rupture strength σ (%)	Change in elongation at rupture ε (%)
On irradiation with waves in the 300–320 mμ region.				
Without additions	—0	200	65	0
Dixanthylene	0·1	110	74	−10
Salol	0·1	200	89	+25
,,	2·0	110	80	−20
o-Oxybenzaldazine	0·1	200	67	−15
2-(*o*-Oxyphenyl)benzoxazole	0·1	200	110	0
,,	0·1	500	130	0
,,	2·0	200	110	−92
β-Methylumbellipherone	0·1	200	85	0
5,7-Dioxy-4-methylcumarene	0·1	200	120	−15
3-Acetylcumarene	0·1	200	75	+15
N-methyltoluenesulphamide	0·1	110	50	−80
,,	2·0	110	66	−15
1,4-Diphenylbutadiene	0·1	200	75	0
Diethyl 2,5-dioxyterephthalate	0·1	200	75	−20
On irradiation with the integrated radiation from a mercury-quartz lamp.				
Without additions	0	100	52	−96
Dixanthylene	0·1	50	brittle	
Salol	0·1	105	57	−75
,,	2·0	121	80	−92
o-Oxybenzaldazine	0·1	100	brittle	
2-(*o*-Oxyphenyl)benzoxazole	0·1	100	65	−65
,,	2·0	141	120	−95
β-Methylumbellipherone	0·1	100	70	−77
5,7-Dioxy-4-methylcumarene	0·1	100	65	−94
3-Acetylcumarene	0·1	100	35	−95
N-Methyltoluenesulphamide	0·1	50	80*	−97
,,	2·0	50	80*	−97·5
1,4-Diphenylbutadiene	0·1	120	90*	−92
Diethyl 2,5-dioxyterephthalate	0·1	100	100*	−94

* Tests performed at a speed of 0·6 mm/sec.

Irradiation of the film specimens was carried out in the conditions indicated in previous papers. For irradiation both the integrated mercury-quartz radiation of a PRK-2 lamp and light of 300–320 mμ wavelength, which was separated out with liqiud filters, were used. The duration of irradiation was 100–150 hr and in some experiments the duration was increased to 500 hr.

Mechanical testing of the specimens was carried out on a dynamometer of the Polyani type. The speed of rupture of the specimes amounted to 0·6 and 0·074 mm/sec. The absorption spectra were studied on a spectrophotometer with a fast recording attachment.

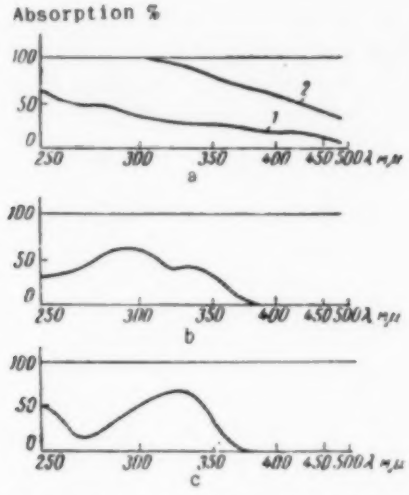

FIG. 1. Absorption spectra. (a) Polyamide anide G-669 film, (1) unirradiated, (2) irradiated for 40 hr with integrated radiation from a PRK-2 lamp; (b) 5,7-dioxy-4-methylcumarene; (c) 3-acetylcumarene.

DISCUSSION OF THE RESULTS

The results obtaind show that irradiation of the polyamide film by mercury-quartz radiation for 100 hr leads to a decrease in the strength of the specimen by 45–50 per cent and in the relative elongation—of up to 10–12 per cent. Considerably smaller changes in the mechanical properties are observed when the anide G-669 films are irradiated with light of 300–320 mμ wavelength. A specimen irradiated for 200 hr shows practically no change in relative elongation. The variation in the values did not exceed ±5–10 per cent of the initial value. The rupture strength of the specimen decreased somewhat, amounting to 65 per cent of the initial value after 200 hr of irradiation. The absorption spectrum also changed considerably (see Fig. 1).

Low-molecular-weight compounds had a marked influence on the change in the mechanical properties of the films under the action of radiation. The Table contains results of tests on the mechanical properties of films obtained on rupturing the specimens on the dynamometer with a speed of 0·074 mm/sec. 2-(*o*-oxyphenyl)benzoxazole added to the film in an amount of 0·1 per cent of the weight of polyamide exhibited a very marked effect. This was especially clearly observed in the irradiation of the polyamide with 300–320 m μ waves. A specimen

of film with this addition did not alter its initial value of relative elongation after 200 hr of irradiation and the strength of the specimens even increased. A still greater increase was observed for films irradiated in the same conditions for 500 hr. At the same time the relative elongation hardly changed. Irradiation of the same specimen in an atmosphere of nitrogen showed that in these conditions the polyamide loses its elasticity to a greater degree than on irradiation in air; at the same time the strength of the film increases. Thus, 2-(*o*-oxyphenyl)benzoxazolé added to a film of anide G-669 in an amount of 0·1 per cent retards the destruction process. This experimental fact is in agreement with the observation of the protective action of 2-(*o*-oxyphenyl)benzoxazole on the photochemical destruction of solutions of anide G-669 made previously [1].

At the same time it appeared that an increase in the concentration of 2-(*o*-oxyphenyl)benzoxazole in the film of polyamide to 2 per cent has a rather different effect on the destruction process of this polyamide. On irradiation of a specimen with this content with unfiltered mercury-quartz radiation a sharp decrease in the value of the rupture elongation was revealed. Replacement of the unfiltered light by filtered light hardly changed anything. The rupture strength of the specimen in both cases increase by 10–20 per cent compared with the initial value. This change in the mechanical properties of the film indicates the main course of the cross-linking process which does not decrease even on irradiating specimens of the polyamide with 300–320 mμ light. Thus, an increase in the concentration of 2-(*o*-oxyphenyl)benzoxazole in the film influences its destruction under the action of utlra-violet radiation unfavourably.

An analogous observation was made for another addition—salol; this substance, introduced into the film in a 0·1 wt.% quantity, has a protective action.

Experiment showed that after 200 hr of irradiation by filtered light the rupture elongation of the specimen of polyamide contain 0·1% salol increased by 25 per cent, while only 10 per cent of the rupture strength is lost. At the same time an increase in the concentration of salol in the film to 2 per cent produces a considerable cross-linking process, as was observed on irradiation of the specimen of polyamide with this addition by filtered light for 110 hr. In this case the decrease in rupture strength and elongation amounts to 20 per cent.

A protective action in the photochemical destruction process of G-669 is shown by β-methylumbellipherone. The destruction of the polyamide specimen containing 0·1 per cent of this addition takes place considerably more slowly than was observed in specimens not containing this addition. This was revealed most clearly in irradiation of the polyamide with 300–320 mμ light. The performance of the experiment in a nitrogen atmosphere leads to a still smaller destruction of the polyamide.

Some retardation in the destruction of anide G-669 is produced by 5,7-dioxy-4-methylcumarene used in 0·1% concentration. The protective influence of this substance was observed in irradiating polyamide specimens containing this addition with 300–320 mμ light. As a result a specimen with a somewhat increased

rupture strength with an insignificant decrease in rupture elongation was obtained. However, no influence was noted for this addition on irradiating films with mercury-quartz radiation. In this case the specimen behaved like the original polyamide without any addition. One may consider that in these circumstances 5,7-dioxy-4-methylcumarene decomposes rapidly under the influence of the radiation. 1,4-diphenylbutadiene and diethyl 2,5-dioxyterephthalate also retard the destruction of the polyamide when it is irradiated with 300–320 mμ light. It was found that with an addition of 1,4-diphenylbutadiene the rupture strength of the specimen decreases somewhat after irradiation with 300–320 mμ light for 200 hr, while elongation practically does not change. The addition of diethyl 2,5-dioxyterephthalate slightly decreases the value of the rupture elongation while slightly raising the strength.

Both compounds were only used in concentrations of 0·1 per cent of the weight of polyamide. The addition of 0·1% 3-acetylcumarene to a film of anide G-669 somewhat protects the polyamide from destruction by 300–320 mμ wavelength radiation. In this case a specimen with increased values of rupture strength and elongation compared with a specimen of polyamide without additions was obtained. However, the mechanical properties of the specimen with an addition of 3-acetylcumarene become markedly worse in comparison with polyamide not containing an addition, if it is irradiated with unfiltered mercury-quartz radiation. Apparently, under the influence of intense radiation 3-acetylcumarene is destroyed with the formation of reactive radicals which produce an intensification of the destruction process of the polyamide.

Two other compounds used as additions to films of the polyamide showed a considerable sensitizing effect. To these compounds belong 2-oxybenzaldazine and dixanthylene; both substances were used in 0·1 per cent concentration. For a specimen containing an addition of the former compound it was found that after 100 hr of irradiation with mercury-quartz radiation it became so brittle that it could not be tested on a dynamometer; a very considerable decrease in the rupture elongation was observed even after 25 hr of irradiation. These results confirm our observations [1] on the sensitizing influence of 2-oxybenzaldazine.

Dixanthylene showed an even sharper sensitizing action. The polyamide specimen with this addition becomes unsuitable for testing as a result of its great brittleness after 50 hr of irradiation with mercury-quartz radiation. Irradiation of the polyamide specimen with this additive with 300–320 mμ radiation produces a somewhat smaller, but nevertheless very considerable destruction. The experimental data permit one to draw conclusions concerning both the above compounds under the influence of radiation with the formation of free radicals which accelerate the destruction of the polyamide. These observations made in the case of dixanthylene confirm our results obtained earlier in studying the photochemical destruction of polystyrene [2], but somewhat contradict the results obtained in studying the photochemical destruction of solutions of anide G-669. We think that this discrepancy can be explained by the conditions to which the

polyamide was subject during irradiation and it is without doubt that dixanthylene does not break down so quickly in a solvent as in the solid state.

The last of the substances used—N-methyltoluenesulphamide—exhibits an accelerating influence on the photochemical destruction of anide G-669 which is especially marked for mercury-quartz radiation. At the same time it should be noted that an increase in the concentration of this additive in the film is little revealed in an increase in the sensitizing effect. It is possible that the reason for this lies in the plasticizing influence of the additive.

The results obtained permit one to say that of the low-molecular-weight compounds used 2-(*o*-oxyphenyl) benzoxazole, salol and *β*-methyl-umbellipherone have a protective influence. These substances slow down the photochemical destruction of the polyamide anide G-669 during irradiation with mercury-quartz radiation. For irradiation with filtered radiation of 300–320 mμ wavelength, besides the compounds enumerated, 5,7-dioxy-4-methylcumarene, 3-acetylcumarene, 1,4-diphenylbutadiene and diethyl 2,5-dioxyterephthalate have a protective influence.

Of the group of compounds named the three substances which are derivatives of cumarene have related structures. It is possible that other derivatives of it not studied in the present investigation may act as stabilizers for photochemical destruction. We would like to remark that some of the substances, such as, for example, 1,4-diphenyl-butadiene, salol and 2-(*o*-oxyphenyl)benzoxazole also exhibited a protective action in the investigation of other polymers [2–4], but to a different degree, depending on the individual properties of the latter. The first two substances have inhibiting and screening properties and this explains their protective influence. The inhibiting properties of the third substance—2-(*o*-oxyphenyl) benzoxazole—were not studied; it is possible that it is also an inhibitor. The ability to luminesce, as we have already remarked several times, is not directly connected with a stabilizing quality of the addition, as has been observed in the case of such intense luminophors as dixanthylene and 2-oxybenzaldazine. As it turned out, they markedly accelerated the destruction of the polymer (in films). We therefore suppose that the use of luminophors as protective agents for polymers is only useful if the given luminophor can act as a free radical inhibitor and ultra-violet screen in the absorption range of the polymer.

The authors wish to express their gratitude to I. V. Obreimov, I. Ia. Kachkurova, G. L. Slonimskii, T. A. Dikareva and L. Z. Rogovina for assistance in the carrying out of the spectral and mechanical tests.

CONCLUSIONS

(1) The existence of photochemical destruction in films of anide G-669 on irradiation with mercury-quartz radiation has been demonstrated.

(2) On irradiating films of anide G-669 with 300–320 mμ radiation the photochemical destruction becomes markedly smaller.

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(3) As additions which retard the photochemical destruction process of anide G-669 one may specify 2-(*o*-oxyphenyl)benzoxazole, salol, *β*-methylumbelliferone, 1,4-diphenylbutadiene, 5,7-dioxy-4-methylcumarene, 3-acetylcumarene, diethyl 2,5-dioxyterephthalate; the best protective action is exhibited by 2-(*o*-oxyphenyl)benzoxazole.

(4) It has been shown that the ability of substances to luminesce is not directly connected with the protective action of the substances used.

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AN ELECTRONIC PARAMAGNETIC RESONANCE STUDY OF THE RADICALS FORMED IN FAST ELECTRON IRRADIATION OF POLYETHYLENE*

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(*Received* 4 *May* 1959)

THE influence of ionizing radiations on polymers has recently been the subject of intensive investigations. In this connexion polyethylene has been studied in the greatest detail. It has been established that irradiation of polyethylene leads to the formation of crosslinkages between the molecules of the polymer and to the appearance of double bonds, and also to the destruction of the polymer molecules. These processes are accompanied by the evolution of gases, ~96 per cent of which is composed of hydrogen and the remainder of hydrocarbons, mainly of low molecular weight.

In spite of the large number of papers devoted to the investigation of the effect of ionizing radiation on polyethylene, the mechanism of the radiation-chemical process in polyethylene has not been finally established. In particular, the problem of the role of radicals in radiation-chemical transformations is discussed in the literature from very varied points of view [1-7].

Recently the formation of radicals when polyethylene is acted on by ionizing radiations has been recorded directly by means of electronic paramagnetic resonance (EPR). It has been established [8–9] that irradiation of polyethylene at 77°K leads to the formation of the $-CH_2-CH-CH_2-$ radical (I). The spectrum of this radical consists of six components of hyperfine structure with a separation of about 30 oersteds which corresponds to the interaction of an unpaired electron with five protons situated in α and β positions with respect to the free valency.

On raising the specimen to room temperature [8] the spectrum of radical (I) disappears and the spectrum of another radical (II) consisting of an uneven number of components with a separation of ~14 oersteds is observed. A spectrum of this type is revealed after irradiating polyethylene at room temperature [10]. The direct observation of the EPR signal in the irradiation of a specimen of polyethylene by fast electrons [11] permits one to record the formation of radical (I) at room temperature. When irradiation ceases the spectrum of radical (II)

* Vysokomol. soedin. **1**: No. 8, 1182–1193, 1959.

is observed. In addition to radicals of type (I) and (II) peroxide type radicals may arise in polyethylene irradiated in the presence of oxygen [10] which give a single unsymmetrical line in the EPR spectrum.

The use of the EPR method for the quantitative investigation of the formation and transformation of radicals may give information regarding the role of radical reactions in the radiation-chemical changes in polyethylene.

In the present work an attempt has been made to undertake such an investigation and a qualitative comparison of the behaviour of radicals in polyethylene specimens with different physico-chemical properties has been made.

THE MEASUREMENT TECHNIQUE

The EPR spectra of the radicals formed on irradiating polyethylene with fast electrons were recorded by a spectrometer with high-frequency modulation of the magnetic field [12] working at a frequency of ~9400 Mc/s.

A rectangular resonator of the H-type with a Q-factor of ~1000 was placed in the field of the electromagnet, the pole piece of which had an aperture for introducing a beam of electrons with an energy of 1·6 MeV into the resonator. This arrangement permitted one to record the EPR spectrum directly during irradiation of the specimen under investigation and to perform kinetic measurements of the accumulation and decay of radicals in solid substances. The sensitivity of the equipment amounted to $\sim 3 \times 10^{15}$ diphenylpicrylhydrazyl radicals in observing the EPR spectrum on an oscillograph. The resolving power was fixed by the inhomogeneity of the magnetic field which amounted to 1·5 oersteds for a specimen thickness of 2 mm. All the equipment, with the exception of the generator for the high-frequency modulation of the magnetic field, was situated in a special space which guaranteed protection from X-rays. The magnetic field of the spectrometer was remotely controlled. The high-frequency power was supplied to and conducted away from the resonator by rectangular wave guides of overall length 25 m.

For performing kinetic measurements the EPR spectra were recorded every 30 sec in the form of the first derivative on an EPP-09 recorder. Possible variations in the amplification factor of the spectrometer were at the same time taken into account by means of a signal from a standard which was registered along with the signal from the specimen during the experiment. As a standard for checking the amplification factor we used a monocrystal of the paramagnetic salt $CuCl_2 \cdot 2H_2O$, the spectrum of which does not coincide with the spectrum of the radicals under investigation for a certain orientation of the magnetic field. The determination of the absolute concentration of radicals in the specimen was carried out by comparing the intensities of the EPR signals from the specimen and a standard with a known quantity of paramagnetic particles placed in the resonator instead of the specimen. The intensity of the signal was determined by means of double intergation of the derivative of the absorption line.

As standards for measuring the concentrations single crystals of $CuCl_2 \cdot 2H_2O$ weighting about 1 mg were used. In calculating the concentrations the Curie temperature for the radicals in polyethylene and for $CuCl_2 \cdot 2H_2O$ were assumed equal to 0°K. In order to avoid saturation of the signal from the specimen the level of the high-frequency power was made sufficiently low.

The energy absorbed in the polyethylene was determined by measuring the strength of the electron current falling on the specimen. The electron retarding capacity in polyethylene for an electron energy of 1·6 MeV was taken as equal to 1·91 MeV/g/cm². It was obtained from the well-known retarding capacity for water (1·85 MeV/g/cm²) taking account of the difference in the ratio of the charge to mass for carbon and oxygen atoms. The radiation yield of radicals G was measured in terms of the number of radicals formed per 100 eV of absorbed. The total error in the determination of the radiation yield according to our estimation amounts to 20–30 per cent. The specimens investigated were prepared in the form of tablets of 3 or 5 mm diameter and ~2 mm thickness and were introduced into the resonator on the end of a thermocouple. The defocussing of the electron beam guaranteed the constancy of the electron current with time and the uniformity of the dose distribution over the specimen. The temperature of the specimen was kept in the range +150°C to −180°C with an accuracy of ~1°C by bathing the specimen in a jet of nitrogen or air.

All the quantitative kinetic experiments in the present work were performed on specimens of granulated high-pressure polyethylene. The qualitative observations of the behaviour of the radicals were carried out on 14 different specimens, including 5 specimens of high-pressure polyethylene, 1 specimen of polyethylene with a commercial stabilizer, 5 low-pressure polyethylene specimens, 2 specimens of radiation polyethylene and 1 specimen of polymethylene.

EXPERIMENTAL RESULTS

The observations of the EPR spectra of high-pressure polyethylene made by us actually during irradiation showed the following. At low temperatures (from 0° to −100°C) irradiation leads to the appearance of radical (I) (Fig. 1a). At high temperatures (about +50°C) the spectrum of radical (II) is observed. In both cases the form of the EPR spectrum does not change after irradiation stops. In the temperature range around room temperature a picture which is a superimposition of the spectra of radicals (I) and (II) is observed. An intense radical (I) signal can only be recorded in the initial period of irradiation. After irradiation stops the signal from radical (I) weakens and the spectrum of radical (II) is observed. We also observed the spectrum of radical (II) after heating a specimen irradiated at low temperature (Fig. 2a). It is interesting to note that the hyperfine structure of the spectrum in this case is resolved better than for irradiation at high temperature.

The accumulation of radicals at low temperatures. The kinetics of radical accumulation were recorded at temperatures of −16, −45, −68 and −95°C and for a radiation dosage level of about 0·5 Mrad/sec with the specimen bathed

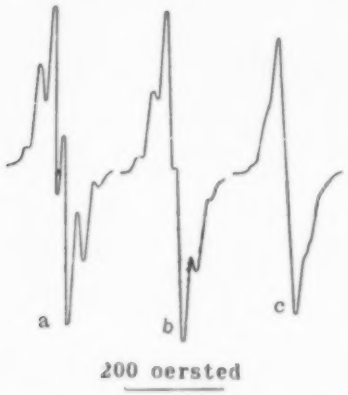


FIG. 1. The change in the form of the EPR spectrum of polyethylene with irradiation at −95°C. The spectra a, b and c are taken at the corresponding points on the curve shown in Fig. 3.

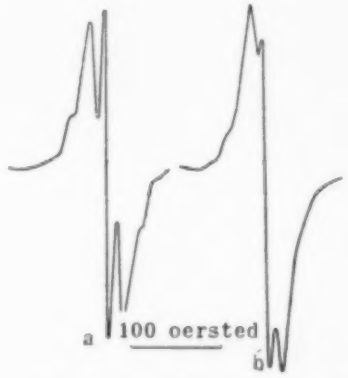


FIG. 2. The EPR spectrum of irradiated polyethylene; (a) at −90°C; (b) − at +70°C.

in a jet of nitrogen. The maximum total dose given to the specimen amounted to 1000 Mrad. Observation of the shape of the EPR signal showed that in the course of irradiation the form of the spectrum changes: at first the characteristic spectrum of radical (I) is observed and then the components of the hyperfine structure begin to broaden and for sufficiently large doses the structure of the spectrum is almost completely blurred (Fig. 1a, b, c). In Fig. 3 the increase in the amplitude h of the first derivative of the EPR signal during irradiation at a temperature of −95°C is shown.

In spite of the fact that the shape of the signal changes, this curve conveys the course of the increase in the concentration of radicals in the specimen quite well. Double integration of the EPR signal at the beginning and end of irradiation shows that the maximum correction associated with the change in the shape of the signal does not exceed 10 per cent. As is evident from the Figure, the accumulation of radicals proceeds linearly up to ~10 Mrad, but considerably slows down for large doses. For a dose of 640 Mrad and a temperature of −95°C, $2{\cdot}5\times10^{20}$ radicals accumulate in a gram of polyethylene (0·6 per cent of the number of CH_2-groups). After the cessation of irradiation the concentration of radicals at this temperature falls markedly in the course of some tens of minutes.

The curves for the accumulation of radicals at other temperatures have qualitatively the same nature as the curve shown in Fig. 3, but at higher tem-

peratures smaller concentrations of radicals accumulate. Thus, for a dose of 640 Mrad the concentration of radicals reached at −16°C proved to be a factor of 3 less than at −95°C.

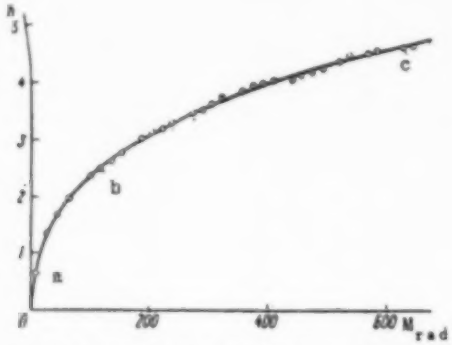


FIG. 3. The increase in the amplitude h of the first derivative of the EPR signal in the process of irradiation at −95°C.

Variation of the radiation dosage level between 0·1 and 0·5 Mrad/sec showed that for temperatures around −100°C the course of the accumulation curve practically does not depend on the dosage level.

In Fig. 4 the initial part of the accumulation curve for radical (I) taken for a temperature of −81°C and a dosage level of about $1{\cdot}2\times10^{4}$ Mrad/sec

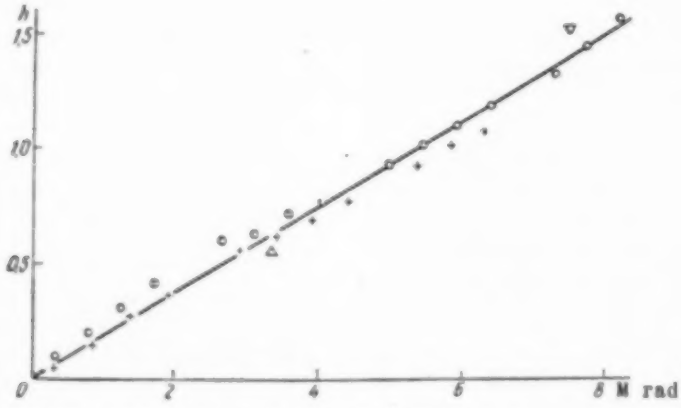


FIG. 4. The initial section of the radical accumulation curve at −81°C.

is shown. The points denoted by different signs in the figure were obtained in different experiments. From these data the radiation yield for radical (I) was found to be $G_1=2{\cdot}9\pm0{\cdot}6$ radicals per 100 eV.

The accumulation of radicals at high temperatures. In Fig. 5 the radical accumulation curve for polyethylene in a stream of air at 50°C and a dosage level

of 0·25 Mrad/sec is shown. For doses of 100 Mrad the characteristic spectrum of radical (II) is observed in these conditions (Figure 2b), but for large doses the structure begins to become markedly blurred. In spite of some changes in

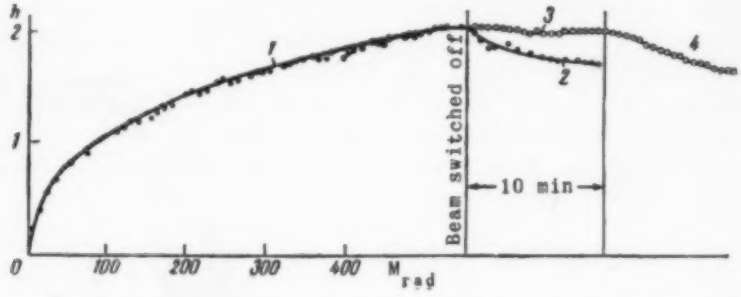


FIG. 5. The behaviour of radicals in polyethylene at +50°C: (1) and (2) The accumulation and decay of radicals for irradiation in air, (3) and (4) The behaviour of radicals after irradiation in vacuum when the specimen is kept in vacuum (3) and in air (4).

the shape of the EPR signal, measurements of the amplitude h of the signal, as in the case of low temperatures, permit one to study the course of the accumulation of radicals.

The kinetics of radical accumulation has qualitatively the same nature as at low temperatures, but at high temperatures a considerably smaller quantity of radicals is formed. For dose of 550 Mrad and a temperature of +50°C about 10^{19} radicals accumulate in a gram of polyethylene. The radiation yield of radical (II) determined at a temperature or +50°C and a dosing level of 0·1 Mrad/sec from the initial part of the accumulation curve amounts to $G_{II}=0{\cdot}16$ per 100 eV.

In Fig. 5 it is shown that after the cessation of irradiation in air a decrease in the concentration of radicals takes place (curve 2). A control experiment with a specimen irradiated in vacuum with a dose of 450 Mrad showed that after the cessation of irradiation the concentration of radicals practically does not fall the specimen is situated in vacuum (curve 3, the initial concentration of radicals in the specimens irradiated in air and vacuum were arbitrarily taken as identical). If one allows air to get at the specimen a fall in the concentration of radicals takes place (curve 4).

The behaviour of radicals in preliminarily irradiated specimens. In the experiments described in the present section use was made of specimens preliminarily irradiated with a certain dose D_0 and then heated at a temperature of about +120°C until the radicals completely disappeared. The form of the EPR spectra obtained after irradiating such specimens with a dose $D \ll D_0$ considerably depends on the size of the dose of preliminary irradiation D_0. For $D_0 \lesssim 100$ Mrad the characteristic spectrum of radical (I) is observed at low temperatures

and of radical (II) at high temperatures. For large D_0 the hyperfine structure of the spectra are blurred and almost completely disappear for $D_0 \approx 500$ Mrad.

Experiments showed that preliminary irradiation has a weak influence on the accumulation of radicals at low temperatures. On the other hand, at high temperature the kinetics of accumulation change considerably. In Fig. 6 curves for the accumulation of radicals in an original unirradiated specimen and a preliminarily irradiated specimen are shown. As is evident from the Figure the preliminary irradiation considerably increase the radiation yield of radicals at the initial stage of irradiation. It was shown by a special control experiment that a preliminary heating of the specimen to the melting point has no influence on the kinetics of radical accumulation at high temperatures. The change in the kinetics is thus completely due to the preliminary irradiation.

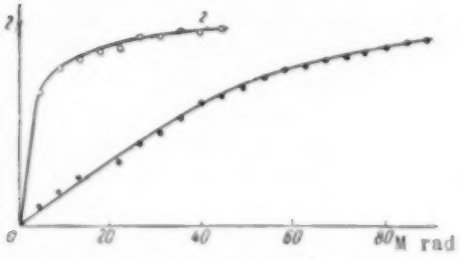


FIG. 6. The accumulation of radicals at +80°C: (1) In an initial sample; (2) In a specimen preliminarily irradiated with a dose of 100 Mrad and heated at +120°C.

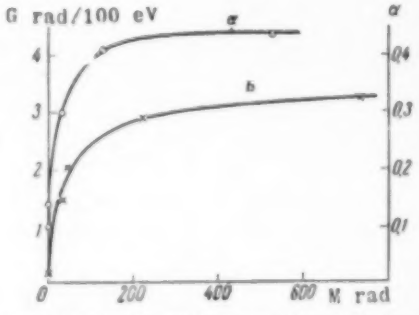


FIG. 7. The dependence of the radiation yield of radicals G at +50°C and the quantity α on the dose of preliminary irradiation.

In order to quantitatively characterize the influence of the preliminary irradiation on the kinetics of radical formation at high temperatures two series of experiments were arranged. In the first series the dependence of the radiation yield of radicals at a temperature of +50°C on the preliminary radiation dose D_0, which was supplied to the specimen at $T = +50$°C, was determined (curve G in Fig. 7). The radiation yield was determined from the initial linear section of the accumulation curve which was taken for doses up to $D \ll D_0$. As is evident from Fig. 7, the radiation yield G increases with D_0, approaching $G = 3{\cdot}2$ radicals per 100 eV. In the second series of experiments the preliminary irradiation was carried out at −40°C. After heating to +120°C these specimens were irradiated at −40°C with a dose of 3 Mrad and were then heated to +40°C. On doing this part of the radicals accumulated at −40°C recombined and only the stable radical (II) remained.

In the experiment the ratio α of the number of radicals stable at room temperature to the number or radicals formed at low temperature was measured. The results of the experiments, which are reproduced in Fig. 7 (curve α), show

that α increases with D_0 in approximately the same way as G, asymptotically approaching a constant value. It is interesting to note that α tends to a value of 0·4 and not 1, i.e. for very large D_0 part of the radicals do recombine on unfreezing the specimen.

Observation of the recombination of radicals at high temperatures showed that the stability of radical (II) increases considerably with increase in the dose of preliminary irradiation. In experiments carried out in vacuum it was found that in specimens irradiated with a small dose at room temperature, heating at a temperature of +95°C for several minutes leads to a complete disappearance of radicals, while in a specimen which has received a dose of about 1000 Mrad, the radicals do not completely recombine even on heating to +160°C. At the same time experiments showed that preliminary irradiation has no important influence on the stability of radical (I).

Experiments with various samples of polyethylene. In all the experiments with various samples of polyethylene we observed quantitatively the same picture, viz., irradiation at low temperatures leads to the appearance of radical (I); on heating the sample in a certain range of temperature the spectrum of radical (I) disappears and the spectrum of radical (II) is observed. At the same time it was discovered that the stability of radical (I) in different samples was different. For a qualitative comparison of the stability of radical (I) in different specimens of polyethylene we recorded the EPR spectra after irradiation at a temperature of +25°C with a dose of about 3 Mrad. The criterion of the stability of radical (I) was that its spectrum could be observed in these conditions. In specimens which had a low degree of crystallinity (high-pressure polyethylene) the spectrum of radical (II) is observed in these conditions with a small admixture of radical (I) which rapidly disappears. In highly crystalline specimens (low-pressure polyethylene and polymethylene) the spectrum of radical (I) is observed and its intensity does not fall with time or falls insignificantly. Rapid recombination of radical (I) occurs in low-pressure polyethylene at temperatures from +40°C to 60°C, and in polymethylene at +70°C.

Since all the specimens investigated by us were powders and the specimens of low crystallinity consisted of granules, we arranged experiments to establish whether the degree of dispersion has an influence on the stability of the radicals. It appeared that melting the powders in vacuum and the conversion of the granules to powders by dissolving them in heptane and subsequently precipitating them with methyl alcohol carefully drying them in vacuum has no significant influence on the stability of radical (I). At the same time, if benzene was used as a solvent, it was found that the benzene residues in the high-pressure polyethylene considerably increased the stability of radical (I). In this connexion it is interesting to note that in a specimen of high-pressure polyethylene with an addition of commercial stabilizer the radicals were also very stable. On investigating radiation polyethylene we found that the pressure under which the tablets used in the experiment were pressed had a strong in-

fluence on the stability of radical (I). In the initial unpressed polyethylene which had the form of a flocculent mass, radicals (I) were more stable (at +25°C the spectrum of (I) was observed) than in a specimen pressed under a pressure of 30 atm and which had the form of a semi-transparent plastic (only the spectrum of (II) is observed at +25°C).

DISCUSSION OF THE RESULTS

The nature of the radicals. At the present time it may be considered established that radical (I) is an alkyl radical, $-CH_2-\dot{C}H-CH_2$ [8, 9]. The nature of radical (II) remains an object of discussion [8, 10].

The discovery of a marked increase in the radiation yield of radical (II) by us after preliminary irradiation apparently means that radical (II) is localized at those alterations in the ideal structure which accumulate with irradiation and have the ability to stabilize free radicals. This conclusion allows one to examine the problem of the nature of radical (II) in more detail. The structure of radical (II) must explain the following properties: (1) the change from an even-numbered nature and the decrease in the value of the hyperfine structure spacing of the EPR spectrum by a factor of approximately two in comparison with radical (I); (2) its higher stability compared with radical (I); (3) the influence of preliminary radiation on the rate of accumulation of radical (II).

The hyphothesis put forward in [8] concerning the hydrogen bond between neighbouring polyethylene chains permits one to explain the properties of the spectrum of radical (II), but cannot explain the influence of preliminary irradiation on the accumulation kinetics. In [10] the assumption is made that radical (II) is formed on stabilizing the free valency on a ternary carbon atom and has the structure

$$-CH_2-\dot{C}\begin{matrix}\diagup CH_2-\\ \diagdown CH_2-\end{matrix}.$$

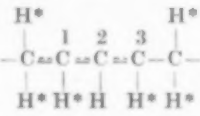
The spectrum of this radical must have an odd number of components, but the decrease in the value of the hyperfine separation by a factor of two in comparison with radical (I) can hardly be explained. Against this assumption concerning the stabilization of the free valency on a ternary carbon atom one can raise the following objections. It is known [14] that in high-pressure polyethylene there is a considerable concentration (2–3 per cent) of ternary carbon atoms even before irradiation. Therefore the additional carbon atoms arising as a result of crosslinking during irradiation ought not to have such an important influence on the accumulation kinetics of radical (II).

It seems to us that the basic properties of radical (II) can be satisfactorily explained by ascribing a structure to it of a radical of the allyl type

$$-CH_2-\dot{C}H-CH=CH-CH_2-.$$

The formation of such a radical requires the presence of transvinylene double bonds, the concentration of which, as is well-known, increases on irradiating

polyethylene. This circumstance permits one to explain the increase in the radiation yield of radical (II) after preliminary irradiation of the specimen. On the other hand the assumption concerning the formation of a radical of the allyl type makes it possible to explain the characteristics of the EPR spectrum of radical (II). It is known from the experimental and theoretical work on the EPR spectrum of allyl-type radicals [9, 15] that in the allyl radical, to which the following structure must be ascribed:



the unpaired electron is distributed symmetrically between carbon atoms 1 and 3, while its density on atom 2 is small. The hydrogen atom joined to carbon atom 2 practically plays no part in the hyperfine splitting of the spectrum. The six atoms marked with asterisks interact with the unpaired electron, which leads to the odd-numbered nature of the spectrum (seven components in the hyperfine structure if all the hydrogen atoms are equivalent). At the same time the distribution of the unpaired electron between atoms 1 and 3 leads to a decrease in the magnitude of the hyperfine splitting by a factor of approximately 2 compared with the splitting for radicals of the alkyl type. In discussing the results we shall in future assume that radical (II) is a radical of the allyl type.

As was noted above, for sufficiently large radiation doses the hyperfine structure of the spectra of radicals (I) and (II) begins to become blurred. This distortion is hardly connected with an increase in the spin–spin broadening on account of the increase in the concentration of radicals since such a blurred hyperfine structure is observed in preliminarily irradiated specimens for quite low concentrations of radicals. Evidently, the main cause of the distortion of the spectra is the change in the structure of polyethylene (crosslinking, formation of double bonds, destruction) with irradiation, as a result of which a considerable quantity of radicals of other types arises along with radical of types (I) and (II). On the other hand, the distortion of the lattice (for example, the change in the valency angles) can also lead to blurring of the hyperfine structure.

The mechanisms of the formation and the accumulation kinetics of radicals. Observation of the stable radical (I) at low temperatures and also the fact that its spectrum may be recorded during irradiation at room temperatures show that the breaking of the C–H bond with the formation of radical (I) is a primary radiation-chemical act. The formation of this radical evidently takes place even at temperatures higher than room temperature, but as a result of the short lifetime the stationary concentration of radical (I) during irradiation in these conditions is insufficient to record its spectrum.

The hydrogen atoms arising when the C–H bonds break have apparently a very short lifetime since even for irradiation at a temperature near to that

of liquid nitrogen we did not succeed in recording the lines of atomic hydrogen. The disappearance of H atoms evidently takes place mainly as a result of the interaction of the H atoms with the polyethylene molecule with the formation of radical (I) and a hydrogen molecule. The role of the recombination reactions of the H atom with radicals and the interaction with double bonds, which is probably unimportant in the initial stages of irradiation, must increase with accumulation of radicals and double bonds.

An interesting feature of the accumulation kinetics of radicals at low temperatures is the considerable decrease in the rate of accumulation for concentrations which are not very high. This decrease is evidently not connected with the recombination of radicals already formed since after irradiation has ceased their concentration does not decrease.

At the same time if one assumes that only two radicals which are immediate neighbours can recombine, one might expect a linear course for the accumulation of radicals up to rather high concentrations.

The cause of the decrease in the accumulation rate may be the recombination reation of the H atom with a radical, the probability of which will increase with accumulation of radicals. On the other hand it is not out of the question that the presence of radicals has an important effect on the mechanism of the radiation-chemical processes, making the splitting-off of an H atom next to an existing radical more probable, resulting in the recombination of two neighbouring radicals. The possibility of such a process was first pointed out in [16].

The preliminary condition for the formation of a radical of the allyl type is the presence of a double bond. We imagine that a radical of the allyl type is formed on the interaction of an alkyl radical obtained in the primary act with a double bond by the reaction:

$$\begin{array}{l} -CH_2-CH-CH_2- \\ -CH_2-CH_2-CH=CH-CH_2- \end{array} \longrightarrow \begin{array}{l} -CH_2-CH_2-CH_2- \\ -CH_2-\dot{C}H-CH=CH-CH_2- \end{array},$$

which occurs at quite high temperatures when radical (I) acquires mobility. In parallel with this reaction radical recombination reactions also take place and therefore the radiation yield of radical (II) is small. Preliminary irradiation of the specimen, by providing an increased concentration of double bonds, increases the probability of the reaction of alkyl radicals with a double bond and leads to an increase in the values of G and α. For sufficiently large doses of preliminary irradiation practically all the radicals formed in the primary act are "captured" at high temperatures by double bonds without having time to recombine and the radiation yield of radicals is near to the radiation yield at $-80°C$.

All that has been said does not exclude the possibility of the formation of the allyl radical in the primary act as a result of the splitting-off of a hydrogen atom next to a double bond. In order that such a process may play an important

part it is however necessary that the probability of the detachment of an H atom next to a double bond should exceed the probability of detachment in a methyl group since the concentration of these groups even in strongly irradiated samples (several hundreds of Mrad) is approximately two orders larger than the concentration of double bonds.

The decrease in the rate of accumulation of allyl radicals takes place at concentrations approximately an order of magnitude less than for the accumulation of alkyl radicals. The fall in the concentration of radical (II) after the cessation of irradiation in air and the absence of a fall in vacuum indicate that radical (II) decays in these circumstances on account of interaction with oxygen. This process may at least partly explain the considerable decrease in the rate of accumulation of radicals. Another apparently more important cause of the slowing down is the tendency for the saturation of the concentration of double bonds noticeable at quite large doses of irradiation [2, 4, 20].

The recombination mechanism and the role of radicals in the cross-linking process. The recombination process takes place when two radicals come together and an opportunity for displacing the free valency is presented. The displacement of a free valency in the solid substance may be realized by two means, viz., (1) as a result of the displacement of the molecules or parts of the molecules containing a free valency relative to one another; (2) by migration of the free valency through the substance. In the case of polyethylene migration may take the form of an H atom jumping to the free valency from neighbouring CH_2—groups.

Rapid recombination of radical (II) takes place at temperatures near the melting point of polyethylene and evidently results from the displacement of the polymer chains. The fact of the increase in the stability of radical (II) in preliminarily irradiated samples agrees well with this assumption: irradiation leads to cross-linking of the polymer molecules and limits their freedom of relative displacement, thus decreasing the possibility of recombination.

To explain the lower stability of radical (I) it is natural to assume the possibility of comparatively easy valency migration in the case of radicals of the alkyl type. This assumption has been expressed in many papers [1, 2, 4, 5] in discussing the mechanism of radiation-chemical processes in polyethylene. It permits one to understand why the allyl radical is more stable. Recombination of the allyl radical by migration of the valency may be made considerably more difficult since this process presupposes as the first act the conversion of the allyl radical to an alkyl radical, which is associated with the expenditure of considerable energy (~15–20 kcal/mole).

The assumption concerning the decisive role of migration in the recombination process of the alkyl radical is confirmed by the circumstance that in preliminarily irradiated specimens this radical is just as stable as in the starting specimens. Preliminary irradiation leads to a limiting of the possibility of the

relative displacement of the polymer chains, but evidently has no important influence on the possibility of valency migration.

The ideas concerning two different mechanisms for radical recombination do not take account of the whole variety of properties of the polyethylene molecules and cannot be considered unambigously proved. According to the data on nuclear resonance in [17-19], in the amorphous phase of polyethylene there is a significantly larger freedom of molecular movement than in the crystalline phase. This means that the stability of the radical may depend essentially on what phase it was formed in. On the other hand, it is known from these same data at temperatures near to room temperature the amorphous phase of high-pressure polythene has the properties of a viscous liquid, and the lattice of the crystallites is also not ideally rigid. Therefore, even at room temperature the possibility of the recombination of the radicals on account of relative displacement of the polymer chains is not excluded, especially in the amorphous part of the polyethylene.

The results obtained by us on the dependence of the stability of radical (I) on the degree of crystallinity of the polyethylene is in qualitative agreement with the results in [20, 21] in which experimental data are obtained which show that the lifetime of the radicals depends on the physical condition of the polyethylene. It is interesting to relate the increase in the stability of the radicals on increasing the crystallinity of the polyethylene to the decrease in the freedom of movement of the segments of the molecule in highly crystalline polyethylene. The limitation of the freedom of this movement, it seems to us, must have a considerable influence not only on the mechanism of recombination, which is associated with the displacement of the polymer chains relative to one another, but also on the possibility of free valency migration. The possibility of movement of segments of the molecule must create more favorable conditions for the attack of the surrounding C—H bonds by the free valency and make the change from the tetrahedral configuration of the bonds to the planar configuration of the bonds in the allyl radical easier. We imagine that a detailed study of the influence of various physico-chemical factors (the degree of crystallinity, the degree of cross-linkage, the presence of impurities, the pressure at which the samples are compressed, etc.) on the lifetime of the radicals together with a parallel observation of proton resonance could give more unambiguous information on the recombination mechanism of radicals in polyethylene.

One might suppose that the recombination of radicals in polyethylene would lead mainly to cross-linking of the polymer molecules and to the formation of double bonds. In the literature, however, there are indications that double bonds are mainly formed as a result of the detachment of molecular hydrogen in the primary radiation-chemical act and that only cross-linking takes place as a result of the recombination of accumulated radicals [20]. Since two radicals are necessary for the formation of one cross-linkage, one may expect that the

radiation yield of radicals will be equal to twice the yield of cross-linkages or will slightly exceed this quantity since the radicals may be partly expended in the formation of bonds inside one molecule (cyclization) or on the formation of double bonds.

As is well-known, the efficiency of the cross-linking process depends on the temperature at which the irradiation of the polyethylene is performed. According to the results quoted in [23] the radiation yield of cross-linkages at −80°C slightly exceeds $G=1$ and from the results in [20] $G=1{\cdot}5$ at the same temperature. These results are in good agreement with the value $G(R)=2{\cdot}9$ at −80°C found by us. There would, however, be little justification for drawing more detailed conclusions from the comparison of these values. The existing methods of determining the number of cross-linkages entail considerable uncertainties, as is shown in particular by the considerable scatter in the experimental results [24]. However, from the single fact that the radiation yield of radicals is comparable to the radiation yield of cross-linkages, it follows without doubt that the subsequent recombination of these accumulated radicals must play a very important, if not decisive role in the cross-linking process under the influence of ionizing radiation.

In conclusion the authors consider it their pleasant duty to thank I. I. Chkheidze for the preparation of standards for the EPR spectrometer measurements. The authors are grateful to V. A. Sergeev and V. L. Karpov who kindly presented the specimens of polymethylene and polyethylene for our experiments.

CONCLUSIONS

(1) On irradiating polyethylene radicals of two types are observed—alkyl (I) and allyl (II).

(2) The difference in the stability of radicals (I) and (II) indicates a difference in their recombination mechanisms and may indicate the possibility of easy valency migration in the case of the alkyl radical (I).

(3) The stability of radical (I) increase with increases in the degree of crystallinity of the polyethylene which may be connected with a decrease in the freedom of molecular movement in highly crystalline samples.

(4) Recombination of the radicals which have accumulated during irradiation must play a considerable role in the cross-linking process of polyethylene.

Translated by N. G. ANDERSON

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MOLECULAR INTERACTIONS IN POLYMER SOLUTIONS— I. THE INFLUENCE OF VOLUME EFFECTS ON THE SECOND VIRIAL COEFFICIENT*

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(*Received* 17 *May* 1959)

THE expression for the second virial coefficient of polymer solutions can be given in the form [1,2]:

$$A_2 = \frac{N_A v}{2M_0^2} F(z) \tag{1}$$

where N_A is Avogadro's number M_0 the molecular weight of a chain segment; v, the effective included volume of the chain segment, which becomes zero at Flory's θ-point,

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{\sqrt{N} v}{a^3}, \tag{2}$$

N is the number of segments in a chain and a, the bond length between neighbouring segments. Using equation (2), equation (1) can be re-written in the form:

$$A_2 = 4\pi^{3/2} N_A \frac{(\overline{R^2})^{3/2}}{M^2} \psi(\alpha), \tag{3}$$

where $\alpha^2 = \overline{R^2}/\overline{R_0^2}$, $\overline{R^2}$ and $\overline{R_0^2}$ are the mean radii of gyration of the chain in the given solvent and in an ideal solvent, respectively, and:

$$\Psi(\alpha) = \frac{z}{\alpha^3} F(z). \tag{4}$$

The relation between α and z is obtained from the theory of intra-molecular interactions of the remote order (volume effects).†

The theory of Flory, Kriegbaum and Orofino [2–4], which substitutes a cloud of segments (whose distribution with respect to the centre of mass is Gaussian) for the real chain, gives [4]:

$$F_{FKO}(z) \cong \frac{4}{3\sqrt{3\pi}} \cdot \frac{\alpha^3}{z} \ln\left(1 + \frac{3\sqrt{3\pi}}{4} \cdot \frac{z}{\alpha^3}\right) = 1 - 1{\cdot}15z + \ldots \tag{5}$$

* Vysokomol. soedin. **1**: No. 8, 1200–1206, 1959.

† The theories used below establish a relation between z and $\alpha_h = (\overline{h^2}/\overline{h_0^2})^{3/2}$ and not between z and $\alpha = (\overline{R^2}/\overline{R_0^2})^{3/2}$. However, since the difference between α and α_h is small (in particular, when z is small, $\alpha^2 = 1 + 134z/105$, and $\alpha_h^2 = 1 + 4z/3$) we will assume in further work that $\alpha \cong \alpha_h$.

The substitution of an exact distribution function (which follows from the Gaussian distribution of the inter-segmental spacing) for the Gaussian distribution, carried out by Isihara and Koyama [7], did not lead to any essential change in the theory [8]. At the same time, the strict theory of the second virial coefficient which applies near the θ-point) [1], [9–11] leads to the function:

$$F_{\text{exact}}(z) = 1 - 2{\cdot}865z + \ldots, \tag{6}$$

which is appreciably different from (5).

To eradicate this discrepancy Kasassa and Markovic[12, 13]substituted a Gaussian distribution with respect to a point of one arbitrary intermolecular contact for the Gaussian distribution of segments with respect of the centre of mass; at the same time calculating approximately the bonding of segments into a chain. Their result, which automatically gave the correct coefficient of z in the expansion of $F(z)$, appears approximately in the form:

$$F_{\text{KM}}(z) \cong \frac{1 - e^{-5{\cdot}68\, z/\alpha^3}}{5{\cdot}68\, z/\alpha^3}. \tag{7}$$

In the derivation of equation (7) the intra-molecular volume effects were not taken directly into consideration. The authors of work [13] calculated approximately the influence of the volume effect on A_2 and assumed that the latter increases α times* the length of the link which connects the neighbouring segments of the chain. As a result of this z/α^3 occurs in equation (7) instead of z. All the same, in practice the volume effects lead to a non-Gaussian distribution function for the inter-segmental spacing, i.e. their influence cannot be related to the change in length of the link [14]. The present work is dedicated to the calculation of this detail within the bounds of the Kasassa–Markovic theory.

CALCULATION OF THE VOLUME EFFECT IN THE FUNCTION $F(z)$

The non-Gaussian form of the distribution function, for the inter-segmental spacing in non-ideal solvents, leads to the fact that various characteristics of the macromolecule, which have the dimension of length, all depend on the volume effect. In preceeding works we have calculated the influence of this condition on the scattering of light [15,16], hydrodynamic properties [16–18] and dimensions [19] of the macromolecules in solution. The non-Gaussian form of the distribution function appears essentially also in the theory of A_2, as can be seen from the examination of the coefficient of z^2 in the expansion of $F(z)$.

The coefficient of z^2 consists of a quantity which depends on triple intermolecular contacts (equal to 9·726 [9]), and of a quantity which depends on the influence of isolated intra-molecular contacts (volume effects) on double inter-molec-

* Theory of Isihara and Koiama agrees with the theory of Flory and Krigbaum, if we first make an analogous assumption.

ular contacts. The trivial effect of this influence, summarized as the change from z to z/α^3 in the linear term, gives the contribution to the coefficient of z^2 as equal to 5·73 [9] (since $\alpha^2=1+4z/3$ [28]). Moreover, the exact effect of the influence of a small proportion of the intra-molecular contacts [10, 11] gave the value of 8·78 as the lower estimate of this contribution. Thus in practice z should be changed not into z/α^3 but into z/α_{eff}^3 (see [19]), where $\alpha_{\text{eff}}>\alpha$. This can be related to the sharpening of the maximum of the distribution function for the inter-segmental spacing, which leads to decreased probability of inter-molecular contacts in comparison with the Gaussian distribution function.

In order to define α_{eff}, it is necessary to estimate the influence of the volume effect on double inter-molecular contacts with the contribution of all the intra-molecular contacts. The general expression for $F(z)$, in an approximation which considers only double inter-molecular contacts, has the form [13]:

$$F(z)=1-\frac{v}{N^2}\sum_{i_1,i_2}\sum_{j_1,j_2}P(O_{j_1,j_1})_{i_1,i_2}+\ldots, \tag{8}$$

where:

$$P(O_{j_1,j_2})_{i_1,i_2}=\int_{\vec{r}_{i_1j_1}=\vec{r}_{i_2j_2}} f(\vec{r}_{i_1j_1})\,f(\vec{r}_{i_2j_2})\,d\vec{r}_{i_1j_1} \tag{9}$$

is the probability of a contact between segments j_1 and j_2 (belonging to molecules 1 and 2), with the condition that segments i_1 and i_2 are found to be in contact: $f(\vec{r}_{ij})$ is the distribution function for the spacing $\vec{r}_{ij}$ between the segments i and j. In the absence of volume effects, $f(\vec{r}_{ij})$ is a Gaussian function, and $P(O_{j_1,\ j_2})_{i_1,i_2}=(3/2\pi a^2)^{3/2}\times(|j_1-i_1|+|j_2-i_2|)^{-3/2}$ [13], which leads to equation (6).

The distribution function $f(\vec{r}_{ij})$, including the volume effect, can be obtained approximately from Peterlin's [21], [22], distribution function for the distance between the ends of the chain [19 [23]], by substituting $(j-i)$ for the last N. We have:

$$f(\vec{r}_{ij})=\left(\frac{3}{2\pi\,|j-i|\,a^2}\right)^{3/2}e^{-\frac{3r_{ij}^2}{2\,|j-i|\,a^2}}\left[1-4z\left(\frac{|j-i|}{N}\right)^{1/2}+\sqrt{6\pi}\,z\,\frac{r_{ij}}{(h_0^2)^{1/2}}\right]. \tag{10}$$

Substituting equation (10) in equations (8) and (9) we obtain:

$$F(z)=1-2{\cdot}865\,z\,(1-4{\cdot}39\,z)+\ldots, \tag{11}$$

That is, the contribution to the coefficient of z^2 depending on the influence of the volume effect on double contacts, is equal to 12·58.

Applying $F(z)$ in the form $1-2{\cdot}865\,z/\alpha_{eff}^3$, we obtain from equation (11):

$$\alpha_{eff}^2=1+2{\cdot}93\,z-\ldots \tag{12}$$

In order to extend this equation to the region of large z, we substitute z/α_{eff}^3 for z in the right hand side of equation (12), where the magnitude of α_{eff}, (obtained

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from work [19]) effectively represents the influence of the degree of the entanglement on intra-molecular volume effects. It is seen that:

$$\alpha_{eff}^3 = 1 + \frac{2{\cdot}93\, z}{\alpha_{eff}^3}, \tag{13}$$

where: [19]

$$\alpha_{eff}^5 - \alpha_{eff}^3 = 1{\cdot}04\, z. \tag{14}$$

Finally, instead of equation (7) we obtain:

$$F(z) \cong \frac{1 - e^{-5{\cdot}68\, z/\alpha_{eff}^3}}{5{\cdot}68\, z/\alpha_{eff}^3}, \tag{15}$$

where α_{eff} is related to equations (13) and (14).

Curve of $\Psi(\alpha)$, constructed from equations (4) and (15) is shown on Fig. 1, where the relation between z and α is defined [19] by equation (14) and the equation:

$$\alpha^5 - \alpha^3 = \frac{4z}{3} \frac{\alpha^3}{\alpha_{eff}^3}, \tag{16}$$

which correctly reproduces the linear and quadratic terms in the expansion of α in powers of z. On the same Figure are shown for comparison the curves of Flory, Kriegbaum and Orofino, $\Psi_{FKO}(\alpha)$, and of Kasassa and Markovic $\Psi_{KM}(\alpha)$, constructed from equations (4), and (5) and (7) respectively. In the Flory, Krigbaum and Orofino theory, the relation between z and α, defined by the following equation [2, 14] was used:

$$\alpha^5 - \alpha^3 = \frac{3\sqrt{3}}{2} z, \tag{17}$$

and in the theory of Kasassa and Markovic—by the equation [20, 24]:

$$\alpha^5 - \alpha^3 = \frac{4z}{3}, \tag{18}$$

which gives correctly the linear term in the expansion of α in terms of z.

DISCUSSION OF RESULTS AND COMPARISON WITH EXPERIMENT

As shown in Fig. 1, the theory of A_2, proposed in this work, agrees almost entirely with the theory of Kasassa and Markovic [13], when α is near to unity, but with an increase in α it leads to much greater values of A_2 (with given chain sizes). When $\alpha \to \infty$ the proposed theory gives $\Psi^\infty = 0{\cdot}58$, from which, when $\alpha \to \infty$, $A_2 M^2/(\overline{R^2})^{3/2} = 7{\cdot}7 \times 10^{24}$. At the same time the theory of Kasassa and Markovic gives $\Psi^\infty = 0{\cdot}18$, from which $\alpha \to \infty$ gives $A_2 M^2/(\overline{R^2})^{3/2} = 2{\cdot}4 \times 10^{24}$.

We would like to point out that, as Olbrecht [9] has shown the lower, limit of the value of Ψ^∞ is 0·28, whence $A_2 M^2/(\overline{R^2})^{3/2} > 3{\cdot}8 \times 10^{24}$. We see that our theory,

as distinct from the theory of Kasassa and Markovic, satisfies this requirement. It is necessary to emphasize, as seen from Fig. 1, that the asymptotic behaviour $\Psi(\alpha) \sim A_2M^2/(R^2)^{3/2}$ is not achieved for normal $\alpha \sim 1{\cdot}5$. Therefore the approximate constancy of the quantity $A_2M/[\eta]$, observed in the experiment, which is approximately proportional to $A_2M^2/(\overline{R^2})^{3/2}$, is explained not by approaching the asymptotic value of Ψ, but by the weak dependence of Ψ on α, found within the limits of the rather considerable experimental error, in the normal range of α (in good solvents). When $\alpha = 1{\cdot}3 - 1{\cdot}5$, $\Psi(\alpha) = 0{\cdot}24 - 0{\cdot}32$. Using Flory's equation:

$$[\eta] = \Phi \cdot 6^{3/2} \frac{(\overline{R^2})^{3/2}}{M}, \tag{19}$$

in which $\Phi = 2{\cdot}1 \times 10^{23}$, (which applies approximately in good solvents [17],[18],) we find that, in this interval of α, $A_2M/[\eta]$ increases from 1·2 to 1·7. The experimental results collected by Olbrecht [9], from a series of authors, and referring approximately to the same interval of α, gives $A_2M/[\eta] = 1{\cdot}4 \pm 0{\cdot}2$. We note that the maximum value of $A_2M/[\eta]$, reached when $\alpha > 1{\cdot}3$, is equal to 0·9, which agrees with the Kasassa–Markovic theory.

On Fig. 1, are also added the experimental results relating to both good and bad solvents. In works on polystyrene [25–27] and poly*iso*butylene [25] in good solvents, A_2, M and $[\eta]$ were measured and α was determined from $[\eta]$ using the equation $\alpha^3 = [\eta]/[\eta]_\theta$ which follows from the equation (19). Values of $[\eta]_\theta$, obtained previously [28], were used in the above. For the polystyrene fraction, for which there was no data, $[\eta]_\theta$ was calculated from the equation $[\eta]_\theta = 0{\cdot}82 \times 10^{-3} \sqrt{M}$, [28]. In practice, as has been shown by us earlier, Flory's coefficient Φ depends on α. Because of this, the use of this equation leads to errors. However, in view of the dependence of Ψ on α, these errors are not important in the given case. This is confirmed both by our discussion and by the agreement between the experimental data of the authors (see Fig. 1) and the works of Shultz [29] on polyvinyl acetate in methylethylketone, and Krigbaum and Carpenter [30], on polystyrene in *cyclo*hexane (in which not $[\eta]$, but R^2 was measured from the scattering of light by Zimm's method). The contribution of the dependence of Φ on α would have led to a small displacement of the experimental points to the right. The values of R^2, necessary for the calculation of $\Psi(\alpha)$ from experimental data for A_2 and M, were calculated by us from equation (19). We see that the experimental results of A_2 for macromolecules in good solvents are described much better by the proposed theory than by the Kasassa–Markovic theory.

The dotted curve on Fig. 1, corresponds to the Flory, Krigbaum, Orofino theory. In the region of common good solvents ($\alpha \sim 1{\cdot}5$) this theory leads to a value of $\Psi(\alpha)$, which is close to that given by our theory. All the same, when α is near to unity and when $\alpha > 2$, the theory of Flory, Krigbaum and Orofino leads to essentially low results. When $\alpha \sim 1$, this theory gives the initial slope of the curve $\Psi(\alpha)$ as approximately half the slope given by the Kasassa–Markovic theory and our theory, which when $\alpha \sim 1$ becomes the same as the exact theory. In other words,

the Flory–Krigbaum–Orofino theory indicates a markedly weaker growth of A_2 with an increase in temperature, near the θ-point, than the exact theory. Fig. 1, and especially Fig. 2, on which the dependence of A_2 on temperature obtained in work [30] is given directly, shows that the experimental data in that region agrees

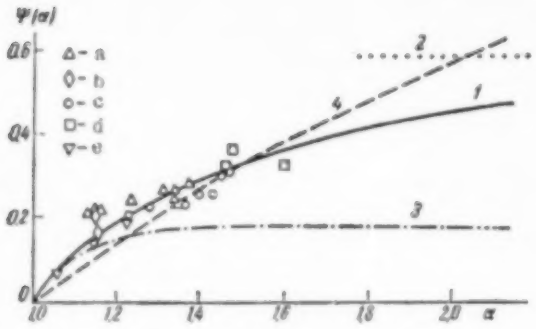

FIG. 1. Relation: $\psi(\alpha) = (^1/_4\pi^{3/2} N_A) A_2 M^2/(\overline{R^2})^{3/2}$ from $\alpha = (\overline{R^2}/\overline{R^2})^{1/2}$ (1) proposed theory; (2) asymptote to this curve; (3) theory Kasassa–Markovic; (4) theory Flory–Krigbaum–Orofino. Experimental results: (a) polystyrene in toluene [25–27]; (b) polystyrene in methylethyl ketone [27]; (c) poly*iso*butylene in *cyclo*hexane [25]; (d) polyvinylacetate in methylethyl ketone [29]; (e) polystyrene in *cyclo*hexane [30].

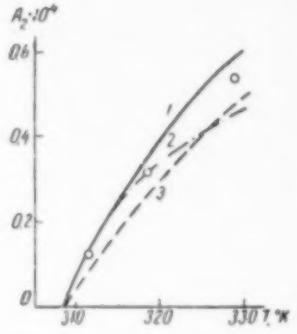

FIG. 2. Dependence of A_2 on temperature near the θ-point: (1) proposed theory; (2) theory Kasassa–Markovic; (3) theory Flory–Krigbaum–Orofino; circles, experimental results (polystyrene in *cyclo*hexane [30].)

with our theory much better than with the Flory–Krigbaum–Orofino theory. Values of α and $\overline{R^2}$, necessary for the construction of the theoretical curves on Fig. 2, were taken from the smoothed—out curve of $R^2(T)$ given in the work [30].* When α is large, the Flory–Krigbaum Orofino theory leads to very large values of $\Psi(\alpha)$, which also does not agree with experiment. Thus from the data of Eskin [31], it can be seen that when $\alpha = 2{\cdot}4$, $\Psi(\alpha) = 0{\cdot}35$, while the Flory–Krigbaum-Orofino theory $\Psi(\alpha) = 0{\cdot}72$ (our theory and the Kasassa–Markovic theory give 0·49 and 0·18, respectively). It is necessary to mention that any increase in the exactness of the Flory–Krigbaum–Orofino theory (exchange of equation (17) by the more exact equation (18), and also the contribution of the non-homogenity of the entanglement) leads to an improved agreement between theory and experiment in the region away from unity.

* In the series of works (see e.g. [13]), which compared the theory with experiment near the θ-point, the values of α, calculated from the equation $\alpha^3 = [\eta]/[\eta]_\theta$, were used. Thus, when Φ depends on α particularly strongly namely near the θ-point [16–18], [30], such comparison becomes untrue.

It is known that A_2 decreases with an increase in the molecular weight, moreover, the experimental data usually appears in the form $A_2 \sim M^{-\gamma}$. From equation (3) we have:

$$\gamma = \frac{1}{2} - \frac{\varepsilon}{2}\left[3 + \frac{d \ln \Psi(\alpha)}{d \ln \alpha}\right], \tag{20}$$

where ε is the degree index in the equation $\overline{R^2} \sim M^{1+\varepsilon}$, which is related to α by the equation $\varepsilon = (\alpha^2 - 1)/(5\alpha^2 - 3)$* [18]. On Fig. 3 is shown the dependence of γ on ε,

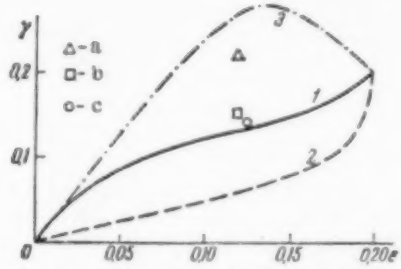

FIG. 3. Dependence of γ on ε. (1) proposed theory; (2) theory Flory–Krigbaum-Orofino; (3) theory Kasassa–Markovic. Experimental results: (a) polystyrene in toluene [25]; (b) the same from [32]; (c) poly*iso*butylene in *cyclo*hexane [25].

which follows from equation (20) and from the expression for $\Psi(\alpha)$ in the theories of Flory–Krigbaum–Orofino, Kasassa–Markowic and ours. On the same sketch are shown experimental results from works [25] and [32], where ε was defined by the dependence of $[\eta]$ on M, in the hypothesis that $[\eta] \sim (R^2)^{3/2}$.† We see the experimental results lie between the theoretical curves obtained from the theories of Kasassa–Markovic and our theory; while theory Flory–Krigbaum–Orofino clearly underestimates the dependence of A_2 on M.

CONCLUSIONS

(1) More exact calculation (when compared with preceeding theories) of the influence of intra-molecular volume effects on the second virial coefficient of polymer solutions leads to an essential change in theory.

(2) Agreement of the values of A_2, obtained in good solvents with given chain dimension, appears to be appreciably better with the proposed theory than with the theory of Kasassa and Markovic, while the dependence of A_2 on molecular weight is noticeably smaller than in the above-mentioned theory.

* This equation follows from the expression $\alpha^5 - \alpha^3 = \text{const.}\ z$. Increasing the exactness of this relation by considering the contribution of non-homogeneous entanglement, [19], has little effect on the relation between ε and α.

† In work [32] the data on $[\eta]$ is absent, therefore the appropriate values of ε were taken from work [25], in which polystyrene in toluene, in a similar molecular weight range, was investigated.

(3) The theory of Flory, Krigbaum and Orofino in the region of normal values of the entanglement coefficient α, leads to the values of A which are near to those predicted by the proposed theory. At the same time, it leads to sharply different results both in bad solvents and in regions of large α and it also predicts much better the weak dependence of A_2 on molecualr weight, than does our theory.

(4) Comparison of several theories of A_2 with experimental results relating to both good and bad solvents, shows that the proposed theory agrees with experiment much better than the theory of Flory–Krigbaum–Orofino, and Casassa–Markowitz.

Translated by Z. KOWSZUN

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POLYMERIZATION OF OLEFINES BY CATALYST COMPLEXES—I. INTERACTION OF ALKYLALUMINIUM CHLORIDES AND TRIETHYLALUMINIUM WITH TITANIUM TETRACHLORIDE*

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(*Received* 20 *May* 1959)

VOL. 1 1960

THE reactions of organo-metallic compounds with derivatives of metals having variable valency have been widely investigated. Increased interest in these reactions resulted from the work of Ziegler, Natta and others; this was closely connected with the problems of composition and structure of complex organo-metallic catalysts.

After their first application, by Ziegler, to the polymerization of ethylene [1], these catalysts were further modified and successfully applied to the polymerization of a whole series of vinyl monomers and diene hydrocarbons. In most catalyst systems of a similar type, a characteristic common to all is the utilisation of a reaction between an organo-metallic compound with a heavy metal derivative (usually a halogen) e.g. Mo, V, Ti, Zr and others.

The catalyst complexes based on aluminium alkyls and titanium chlorides have assumed major importance. Their composition has been studied by a number of authors.

Natta [2] showed that the composition of the products of the reaction between triethylaluminium and titanium tetrachloride depends on the proportions of the reactants and varies with time. Thus the mole ratio of Cl/Ti in the sediment decreases from 2·7 to 0·7 when the ratio $(C_2H_5)_3Al/TiCl_4$ changes from 1 to 4, and the ratio Al/Ti accordingly increases from 0·2 to 0·4. Quantitative data on the influence of temperature and concentration of reactants on the rate of reaction is not given in the above work.

Friedlander and Oita [3] determined the amount of trivalent titanium formed during the reaction of $TiCl_4$ with C_4H_9Li and with $(iso\text{-}C_4H_9)_3Al$, and they have shown that the latter reduces Ti^{4+} to Ti^{3+} faster and more completely. With equimolar proportions of the reactants the reduction to Ti^{3+} proceeds quantitatively with only negligible formation of Ti^{2+}.

* Vysokomol. soedin. 1: No. 8, 1207–1213, 1959.

On examining the mechanism of the reaction, Friedlander proposed the formation of unstable organo-titanium compounds as intermediate products, followed by their homolytic fission with formation of free radicals:

$$TiCl_4 + AlR_3 \rightarrow TiCl_3R + R_2AlCl;$$
$$TiCl_3R \rightarrow TiCl_3 + R^{\cdot},$$
$$2R^{\cdot} \rightarrow R_{(+H)} + R_{(-H)}.$$

Similarly, secondary processes which account for the formation of alkyl-aluminium chlorides can occur. With triethylaluminium (TEA) both diethyl-aluminium chloride (DEA) and monoethylaluminium dichloride (MEA) are formed:

$$(C_2H_5)_2AlCl + TiCl_4 \rightarrow C_2H_5AlCl_2 + TiCl_3 + C_2H_4 + C_2H_6;$$
$$C_2H_5AlCl_2 + TiCl_4 \rightarrow AlCl_3 + TiCl_3 + C_2H_4 + C_2H_6.$$

The composition of the products of the reaction between AlR_3 and titanium tetrachloride will depend on the relative rates of the main and the secondary reactions. Considering that during polymerization of ethylene both TEA and DEA are formed, and that DEA and MEA are formed during the reduction of $TiCl_4$, the study of the above reactions is interesting from the point of view of the influence of the proportions of the components, temperature, and the duration of the reaction on the composition of end products. Moreover, there is evidence that the activated complexes which $TiCl_3$ forms with each of the aluminium alkyls examined here, are not equivalent in their catalytic properties. This may lead to the formation of a polymer which is not homogeneous in structure and in its physico-mechanical properties.

In the first stage of the investigation of the polymerization of ethylene, using a catalyst based on $TiCl_4$ and the aluminium alkyls indicated previously, we have carried out a comparative study of the reduction reactions of Ti^{4+} to Ti^{3+} involving $TiCl_4$, MEA, DEA and TEA. *

EXPERIMENTAL SECTION †

Synthesis of the organo-aluminium compounds was carried out by a method fully described in literature [5, 6, 7]. The substances obtained were distilled under vacuum and analysed to determine the content of ethyl groups, aluminium and chlorine, directly before use.

TEA did not contain chlorine; the ethyl group content was 74 per cent compared with 76·3 per cent, required by theory, which is equivalent to a 5–6 per

* While preparing this work for printing, the work of Kovacs *et al.* [4] in which the system "alkylaluminium-titanium tetrachloride" was studied, was brought to our notice. The results given in it were obtained under non-isothermal conditions, which makes any comparison with our results difficult.

† Experimental part was carried out with the help of Krasnosel'skoi.

cent content of monoethoxy-diethylaluminium. The ethyl group content in DEA was 46·1 per cent (theoretical: 48·2 per cent), in MEA it was 21·6 per cent (theoretical: 22·8 per cent).

The measuring out of components was carried out on the basis of non-oxidized ethyl groups.

The titanium tetrachloride was obtained as a pure reactive compound, which was subjected to a further distillation.

The reaction between alkylaluminium chlorides with titanium tetrachloride was studied both in solution and in the absence of a solvent—for which petroleum ether with a boiling range of 100°C to 115°C was used. The petroleum ether was dried with activated alumina and was re-distilled over metallic sodium.

The reaction of MEA and DEA with titanium tetrachloride, without a solvent, was carried out in an apparatus, shown on Fig. 1. Vessel 1 was heated, *in vacuo* at 250°C, and blown through with nitrogen before use. Into one of the compartments of the vessel titanium chloride was introduced, and into the other—the aluminium compound. The reactants were introduced from the graduated vessels, 2 and the amounts added were determined by a second weighing of the reaction vessel. The filled vessel was placed in a thermostat and it was connected to a system consisting of a U-tube, a gas burette and a hydraulic valve filled with transformer oil. The reagents were brought into contact by careful tilting of the vessel 1.

The reaction between MEA or DEA and titanium tetrachloride, in the absence of a solvent, proceeds with an extraordinary energy—explosively, at room tem-

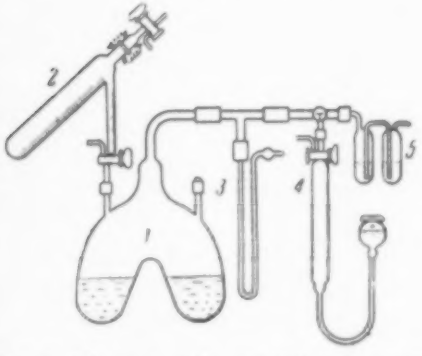

FIG. 1. Diagram of the apparatus for carrying out the reaction in the absence of a solvent. (1) Vessel for mixing the reagents (reaction vessel). (2) Graduated measuring vessel; (3) Manometer; (4) Gas burette; (5) Hydraulic valve.

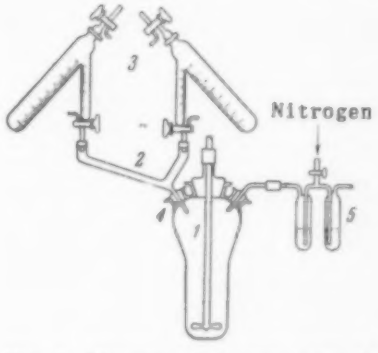

FIG. 2. Diagram of the apparatus for carrying out the reaction in solution. (1) Reactor; (2) Three-way adapter; (3) Graduated measuring vessels; (4) Ground cone and socket joint; (5) Hydraulic valve.

perature. For this reason the reactants were mixed together very slowly, during a period of 15–20 min. As a result of the reaction a dark brown sediment appea-

red and gaseous products, containing ethane and ethylene, were evolved. The presence of the latter, which was determined by absorption in bromine water, depends on the time of contact between the gas and the residue and forms 1 to 10 per cent of the gas. To obtain the yield of titanium trichloride, the contents of the vessel (at the end of the reaction) were acidified with 10 per cent sulphuric acid solution.

At this stage ethane was evolved and a violet solution was obtained. This was transferred, under nitrogen, into a measuring flask from which aliquot samples were taken and were titrated with ferric alum solution, in the presence of ammonium thiocyanate as an indicator.

TABLE 1. REACTIONS OF ORGANO-ALUMINIUM COMPOUNDS WITH TITANIUM TETRACHLORIDE

Organo metallic compound			Titanium tetrachloride		$m \cdot \frac{R_nAlX_{3-n}}{TiCl_4} = n$	Temperature (°C)	Time of experiment	Yield of Ti^{3+} (mol %)
Name	Concentration (g/l.)	volume (ml)	Concentration (g/l.)	volume (ml)				
Monoethylaluminium chloride	7·0	3·0	41·7	5	1:1	20	20 min	20·7
	47·0	3·0	41·7	5	1:1	20	24 hr	50·1
	47·0	3·0	41·7	5	1:1	20	72 ,,	71·3
	47·0	6·0	41·7	5	2:1	20	48 ,,	93·5
	47·0	6·0	41·7	5	2:1	20	72 ,,	100
	47·0	6·0	41·7	5	2:1	80	20 min	98·5
Diethylaluminium chloride	34·4	7·6	41·7	10	1:1	80	20 min	100
	34·4	3·8	41·7	10	0·5:1	80	20 ,,	79·2
	34·4	3·8	41·7	10	0·5:1	20	24 hr	75·1
Triethylaluminium	23·0	5·4	41·7	15	0·33:1	20	20 min	37
	23·0	5·4	41·7	15	0·33:1	80	20 ,,	84
	23·0	10·8	41·7	15	0·67:1	80	20 ,,	100

The reactions in solution were carried out in the apparatus, which is shown in Fig. 2, placed in a thermostat. First the titanium tetrachloride solution (0·22 mol/l.) was measured from the graduated vessel 3 into the reaction vessel 1, through a three-way adapter 2. Then, with the stirrer in operation, the organo-aluminium compound solution was added during 30–40 sec. After this the graduated vessels, 3, were disconnected, together with the adapter, and the reaction mixture was stirred for a given time. Then, 20 ml of 10% sulphuric acid solution, previously blown through with nitrogen and containing an indicator, were introduced through the ground cone, 4. A burette was then attached and the trivalent titanium was titrated until a pink colour appeared. In the process of titration, the violet colour of the solution gradually disappears, and the point of transition to a pink colour is sharp.

In the series of experiments which took a longer time (70 hr or more), the reactions were carried out in sealed tubes which were shaken continuously.

The typical conditions, under which the experiments on reactions in solvents were carried out, are given in the Table.

DISCUSSION OF RESULTS

The rate of reaction between $TiCl_4$ and MEA increases with a rise in temperature. Thus if the reaction at 20°C gives 20 per cent yield of Ti^{3+} in the first 2 hr and the further reaction continues at a decreasing rate until it gives a yield of Ti^{3+} ~ 70 per cent in 3 days (24-hr days), then at 80°C the reaction practically ceases in about 30 min and the yield of Ti^{3+} reaches ~ 80 per cent, with equimolar quantities of reactants (see Fig. 3, curves 1 and 4). Increasing the temperature to 100°C does not lead to any further increase in the yield of Ti^{3+}.

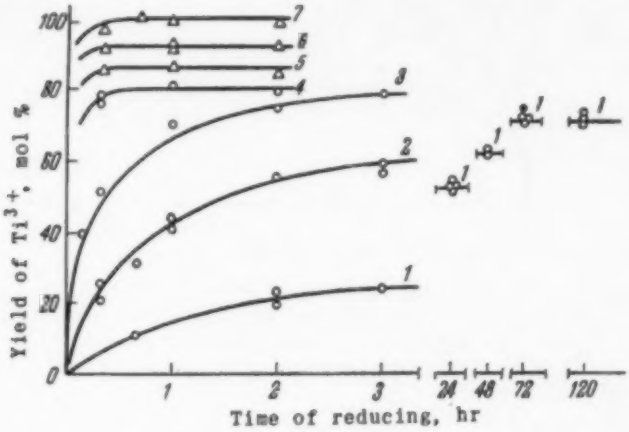

FIG. 3. Reduction of titanium tetrachloride with monoethylaluminium dichloride in solution. $C_2H_5AlCl_2$=0·37mol/l. $TiCl_4$=0·22mol/l. Molar ratio $C_2H_5AlCl_2$: TiCl =n; (1) 20°C, n=1; (2) 40°C, n=1; (3) 60°C, n=1; (4) 80°C, n=1; (5) 80°C, n=1·2; (6) 80°C, n=1·4; (7) 80°C, n=2.

Thus in the reaction of $TiCl_4$ with MEA, incomplete reduction of Ti^{4+} takes place and the upper limit of the yield of Ti^{3+} is ~ 80 per cent when the molar ratio $C_2H_5AlCl_2/TiCl_4$=1. Incomplete utilization of MEA is confirmed also by the fact that the sediment, obtained with a large excess of titanium tetrachloride, evolves hydrocarbon gases on decomposition with water. Apparently, a part of MEA is bound in a co-ordinate complex or is adsorbed by the titanium chlorides. It is also possible that the reaction mixture contains organo-titanium compounds. When these are decomposed with water, the following reaction occurs:

$$TiCl_3R + HO_2 \rightarrow TiCl_3OH + RH.$$

The yield of Ti^{3+} increases with the increase in n: with a two—fold excess of MEA, i.e. when $n=2$, the yield approached 100 per cent (see curves 4, 5, 6 and 7 on Fig. 3).

For the reaction of DEA with $TiCl_4$, similar relations were obtained for the influence of temperature and mole ratio of reactants on the rate of reaction (Fig. 4). At 80°C an 80 per cent yield of trivalent titanium was obtained with $(C_2H_5)_2AlCl/TiCl_4=0{\cdot}5$; complete reduction of tetravalent titanium was obtained when $n=1$ (Fig. 4, curves 4 and 7).

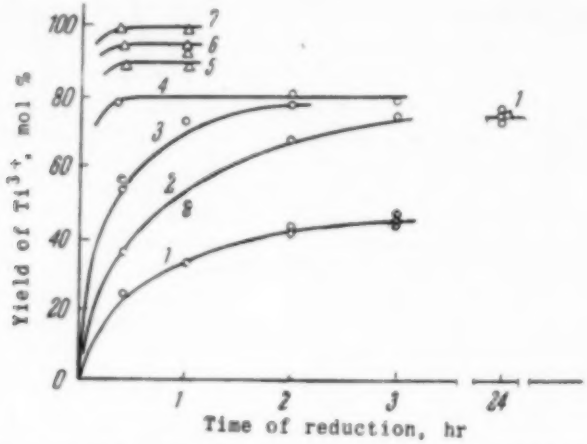

FIG. 4. Reduction of titanium tetrachloride with diethylaluminium chloride in solution. $(C_2H_5)_2AlCl=0{\cdot}28$mol/l. $TiCl_4=0{\cdot}22$ mol/l. Molar ratio: $(C_2H_5)_2AlCl$: : $TiCl_4=n$; (1) 20°C, $n=0{\cdot}5$; (2) 40°C, $n=0{\cdot}5$; (3) 50°C, $n=0{\cdot}5$; (4) 80°C, $n=0{\cdot}5$; (5) 80°C, $n=0{\cdot}6$; (6) 80°C, $n=0{\cdot}7$; (7) 80°C, $n=1{\cdot}0$.

Reduction of $TiCl_4$ at room temperature proceeds faster with DEA than with MEA; however, at 40°C and at higher temperatures the rates of the reactions do not differ appreciably.

The reaction of titanium tetrachloride with TEA proceeds with certain differences. The character of the dependence of the reaction rate on temperature and molar ratio of the reactants remains the same as in examples considered above. When the ratio $(C_2H_5)_3Al/TiCl_4=0{\cdot}33$ (which is equivalent to the ratio $C_2H_5/TiCl_4=0{\cdot}5$ for DEA and $n=1$ for MEA), the limiting yield of trivalent titanium at 80°C is ~ 85 per cent (Fig. 5, curve 4). At room temperature the limiting yield (~ 75 per cent is reached in 6 hr) (Fig. 5, curve 1). At room temperature, it is possible to note that the first of the three ethyl groups in the molecule of TEA is reduced much more easily, than the other two, during the reaction. Thus a yield of ~ 30 per cent of Ti^{3+} was obtained only 2 min after mixing the reactants. This is equivalent to a quantitative conversion of TEA into DEA. The DEA formed reacts further considerably more slowly,

which is indicated by the sharp bend on curve 1, shown on Fig. 5. With an increase in n the yield of the trivalent titanium increases and reaches 100 per cent when $n=0{\cdot}67$ (Fig. 5, curve 5).

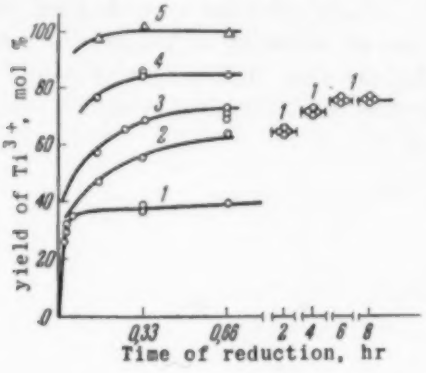

FIG. 5. Reduction of titanium tetrachloride with triethylaluminium in solution: $(C_2H_5)_3Al=0{\cdot}20$ mol/l. $TiCl_4=0{\cdot}22$ mol/l. Molar ratio: $(C_2H_5)_3Al : TiCl_4=n$. (1) 20°C, $n=0{\cdot}33$; (2) 50°C, $n=0{\cdot}33$; (3) 60°C, $n=0{\cdot}33$; (4) 80°C, $n=0{\cdot}33$; (5) 80°C, $n=0{\cdot}67$.

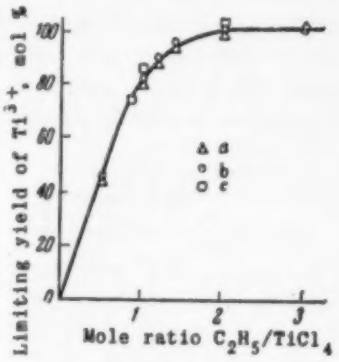

FIG. 6. The dependence of the limiting yield of titanium tetrachloride on the molar ratio: $C_2H_5 : TiCl_4$ at 80°C. (a) $C_2H_5AlCl_2=0{\cdot}37$ mol/l. (b) $(C_2H_5)_2AlCl=0{\cdot}28$ mol/l. (c) $(C_2H_5)_3Al=0{\cdot}20$ mol/l.

Comparison of the results, obtained on MEA, DEA and TEA, show that at 80°C the same limiting yield of trivalent titanium is obtained with the same mole ratio of the active ethyl groups (of the alkylaluminium) to the titanium tetrachloride : $m=C_2H_5/TiCl_4$. Complete reduction of titanium tetrachloride is obtained when $m=2$ (Fig. 6).

CONCLUSIONS

(1) A comparative study has been carried out on the reaction of monoethylaluminium dichloride, diethylaluminium chloride and triethylaluminium with titanium tetrachloride in the temperature range 20°C to 80°C and in various molar proportions.

(2) It has been shown that in all the cases the reaction does not lead to a complete reduction of the organo-aluminium compound—even with an appreciable excess of titanium tetrachloride. This is probably explained by complex formation.

(3) It has been shown that the case of reduction increases in the series: $C_2H_5AlCl_2 < (C_2H_5)_2AlCl < (C_2H_5)_3Al$, moreover, in going from monoethylaluminium chloride to diethylaluminium chloride the change is insignificant,

and from diethylaluminium chloride to triethylaluminium it occurs in a sharp jump. At 80°C the ease of reduction per ethyl group is equal for the three organoaluminium compounds which have been examined.

Translated by Z. KOWSZUN

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AN INVESTIGATION OF THE REACTIVITY TOWARDS FREE RADICALS OF MODEL COMPOUNDS OF SYNTHETIC RUBBERS — I. INTERACTION WITH THE TERTIARY BUTYL RADICAL*

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(*Received* 16 *June* 1959)

THE object of the present investigation is to examine the radical reactions that occur in the cross-linking processes of synthetic rubbers, in model compounds consisting of two polymer links which are differentiated only by the fact that, instead of methylene groups, there are methyl groups in the extremities. The latter, on account of their distance, do not exert a notable influence on the character of the reactions which are responsible for the cross-linking of the polymers and which occur wtih the participation of binary bonds or α-methylene groups.

In order to compare the reactivity in radical reactions of the basic types of synthetic rubbers obtained on the basis of chloroprene, isoprene and divinyl, the following model compounds were synthesized: $CH_3CCl=CHCH_2CH_2CH=CClCH_3$ (1,4–4,1) (I); $CH_3CCl=CHCH_2CH_2CCl=CHCH_3$ (1,4–1,4) (II); $CH_3C(CH_3)=CHCH_2CH_2C(CH_3)=CH(CH_3)$ (1,4–1,4) (III); $CH_3CH=CHCH_2CH(CH_3)-CH=CH_2$ (1,4–1,4) (IV).

Compounds (I) and (II) modelling the basic types of polychloroprene structures with units in 1,4–4,1 combination and 1,4–1,4 combination were first obtained by the present authors. Compound (III) is a model for the structure of polyisoprene with units in 1,4–1,4 combination, and (IV) is a model of the structure of divinyl polymer with units in 1,4–1,2 combination.

Compound (I), modelling polychloroprene with units in 1,4–4,1 combination, was obtained from 1-iod-3-chlorobutene-2 by Mg-organic synthesis:

$$CH_3CCl=CHCH_2I+Mg\rightarrow CH_3CCl=CHCH_2MgI;$$

$$CH_3CCl=CHCH_2MgI+CH_3CCl=CHCH_2I\rightarrow CH_3CCl=CHCH_2CH_2CH=CClCH_3.$$

The structure of compound (I) was demonstrated by infra-red spectroscopy and by chemical methods.

Compound (II) was obtained by condensation of 2-chlorobutadiene-1,3 with 1,3-dichlorobutene-2 in the presence of anhydrous $FeCl_3$ [1] with the consequent

* Vysokomol. soedin. 1: No. 8, 1242–1245, 1959.

reduction of the product of the combination of two molecules of hydrogen in the presence of Ni-Rhenium.

The reaction takes the following form:

$$CH_2CCl=CHCH_2Cl+CH_2=CClCH=CH \xrightarrow{FeCl_3} \quad (V)$$

$$\rightarrow CH_2CCl=CHCH_2CH_2CCl=CHCH_2Cl \xrightarrow{H_2(Ni)} CH_2CCl=CHCH_2CH_2CCl=CHCH_3 .$$

The structure of the intermediate compound (V) has been previously demonstrated by ozonolysis, and that of compound (II) by spectroscopy and chemical methods. Compound (III) modelling 1,4–1,4 polyisoprene was obtained by a method previously described [2].

Numerous attempts to synthesize the compound, $CH_3CH=CHCH_2CH_2CH=CHCH_3$, modelling the structure of divinyl polymer, by the method of Lespilau *et al.* [3], produced negative results and led mainly to the formation of compound (IV), modelling a divinyl polymer with units in 1,4–1,2 combination. Similar results were also obtained using other methods of synthesis. In this respect, the reactivity of the compound in radical reactions has not been investigated.

The interaction of free radicals with the model compounds mentioned may occur in two directions: (1) addition in a binary bond and (2) breakaway of a hydrogen atom from the methylene group arranged in α-position towards the binary bond.

The direction and degree of the course of the reaction with free radicals in unsaturated compounds depends on the position of the binary bond and on the structure of the free radicals. In the past few years this question has been the object of a series of investigations [4,5] which have demonstrated that the addition of free radicals is the basic reaction of unsaturated compounds containing an external binary bond. In the case of olefines having an internal binary bond, the breakaway of hydrogen atoms from the methylene group occurring in α-position to the binary bond is the basic reaction.

An investigation of the reactivity and directions of the reactions of the above mentioned model compounds (I)–(IV) was tested for different radicals. The present paper presents data on the interaction of compounds with only one source of free radicals—the *tert*butyl peroxide $(CH_3)COOC(CH_3)_3$, forming the oxygen-containing radical $(CH_3)_2CO$.

The decomposition of the *tert*butyl peroxide takes place in two stages:

$$1)\quad (CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO^{\cdot} ;$$

$$2)\quad (CH_3)_2CO^{\cdot}+RH \rightarrow (CH_3)_2COH+R^{\cdot}$$

$$\text{or}\qquad (CH_3)_2CO^{\cdot} \rightarrow (CH_3)_2CO+CH^{\cdot}_3 .$$

The kinetics of decomposition has been investigated by Rust *et al.* [6] who showed that decomposition occurs in accordance with a first-order equation of reaction. With a medium containing active hydrogen atoms, trimethylcarbinol is formed, the amount depending on the activity of the hydrogen atom. To a smaller extent acetone is formed.

The reactivity of the compounds studied may be quantitatively considered from the $(CH_3)_3COH/(CH_3)_2CO$ relationship. Infra-red spectroscopy was used for the simultaneous determination of the products of decomposition (acetone, trimethylcarbinol and non-decomposed peroxide). The activity of four molar concentrations of peroxide solutions in the model compounds under consideration (1:1, 1:2, 1:4, and 1:10) was studied. Table 1 presents data obtained in one of the tests for the 1:4 ratio.

TABLE 1. THE INTERACTION OF MODEL COMPOUNDS WITH *tert*BUTYL PEROXIDE

Compound	Trimethylcarbinol acetone
1,4–1,4 polychroroprene model	2·2
1,4–4,1 „ „	3·0
1,4–1,4 polyisoprene „	6·0
1,4–1,2 polybutadiene „	4·3

These data show that the compounds studied may be arranged in the following order according to the reaction activity of the decomposition of hydrogen from the α-methylene group by the *tert*butyl radical:

polyisoprene 1,4–1,4 > polybutadiene 1,4–1,2 > polychloroprene 1,4–4,1 > polychloroprene 1,4–1,4 .

On completion of the tests the unsaturation of the compounds was determined. The presence of only one binary bond was established for the compound modelling the 1,4–1,2 divinyl polymer structure; the addition of radicals took place apparently on the external binary bond. Unsaturation in the other compounds did not vary. This points to the fact that reaction with free radicals only occurred in the α-methylene group.

In addition to the four above mentioned compounds in the reaction with *tert*butyl radicals, vinylcyclohexene – the cyclic dimer of divinyl – was also studied. As a result of the decomposition of peroxide in a divinyl dimer medium, an insoluble and apparently strongly cross-linked rubber-like polymer was formed. The formation of such a polymer is very interesting, but whether it occurs through the combination of cycles or of lateral vinyl groups has not yet been explained.

EXPERIMENTAL SECTION

2,7-dichlorooctadiene-2,6 (I). 1,3-dichlorobutene-2, which was converted into 1-iod-3-chlorobutene-2 with a b.p. of 70°C/18 mm by exchange reaction with NaI or KI in acetone, was used as the starting material, and compound(I) was obtained by Mg-organic synthesis; b.p. 78/100 mm, n_D^{20}1·4830, d_4^{20}1·0566, unsaturation 94 per cent of the theoretical.

Observed: mol. wt. 177·4; Cl (total) 39·5 per cent.

$C_8H_{12}Cl_2$. Calculated: mol. wt. 179; Cl (total) 9·9 per cent.

2,6-dichloroctadene-2,6 (II). To sythesize this compound, freshly dispersed 2,6,8-trichloroctadene-2,6 with the constants as shown [1] was used. In this compound saponified chlorine was hydrogenated in the presence of Ni-rhenium without varying its unsaturation. Compound (II) with b.p. 73°C/10mm, n_D^{20} 1·4680, d_4^{20} 1·0108, unsaturation 96 per cent of the theoretical, was separated by vacuum distillation.

Observed: mol. wt. 174·5; Cl (total) 39·4 per cent.

$C_8H_{12}Cl_2$. Calculated: mol. wt. 179; Cl (total) 39·9 per cent.

Compounds (III) and (IV), as shown above, were obtained by the methods described in references [2,3].

The *tert*butyl peroxide was obtained by the method of Milas and Surgenor [7] from *tert*butyl alcohol and and hydrogen peroxide. A quantity of peroxide was placed in a 5-ml ampoule and diluted with the necessary amount by weight of octadiene. Four molar "peroxide: dimer" ratios were investigated, viz. 1:1, 1:2, 1:4, 1:10. The ampoules were cooled at −70°C, evacuated, blown through with nitrogen, sealed and placed in a thermostat at 135°C for 7·5 hr, after which they were opened and their contents diluted with the necessary amount of absolute CCl_4 for analysis.

Infra-red spectroscopy was used for the quantitative determination of the trimethylcarbinol, acetone and non-disintegrated peroxide.* The determinations were made on the automatic double-beam spectroscope IKS-2 with 1mm long KCl cells. For each component, calibration curves were plotted based on the standard solutions (on average 10) in the co-ordinates: absorption (%)–component concentration. From these data appropriate concentration was found.

TABLE 2. ANALYSIS OF THE DECOMPOSITION PRODUCTS OF *tert*BUTYL PEROXIDE IN THE PRESENCE OF OCTADIENES AT 135°

Octadiene	Peroxide (g)	Decomposition (%)	Obtained		$\frac{(CH_3)_3COH}{(CH_3)_2CO}$
			Trimethylcarbinol	Acetone	
2,7-dichloroctadiene-2,6	0·0582	14	0·026	0·009	3·0
2,6-dichloroctadiene-2,6	0·1553	42	0·0491	0·022	2·3
2,6-dimethyloctadiene-2,6	0·066	16	0·037	0·0056	6·0
5-methylheptadiene-2,6	0·0816	24	0·039	0·009	4·3

CONCLUSIONS

(1) The compounds 2,7-dichloroctadiene-2,6 ($CH_3CCl=CHCH_2CH_2CH=CClCH_3$) and 2,6-dichloroctadiene-2,6, modelling the structure of chloroprene polymers with units in 1,4-4,1 and 1,4-1,4 combination were synthesized for the first time.

(2) A study was made of the tert-butyl radical $(CH_3)_3CO$ with the four unsaturated compounds modelling the structures of chloroprene, isoprene and butadiene polymers.

(3) The following order of reactivities was established for the compounds: polyisoprene 1,4–1,4 > polybutadiene 1,4–1,2 > polychloroprene 1,4–4,1 > polychloroprene 1,4–4,1.

Translated by D.K. BROOKS

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* All the infrared spectroscopy measurements were carried out by G. I. Semenov, senior scientific assistant in the dept. of chemistry of the Voennaia Akademiia Transporta i Tyla.

AN INVESTIGATION OF THE REACTIVITY TOWARDS FREE RADICALS OF MODEL COMPOUNDS OF SYNTHETIC RUBBERS—II. INTERACTION WITH DIPHENYLPICRYLHYDRAZYL*

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(*Received* 16 *June* 1959)

IN the present paper the relative reactivity of the four the model compounds mentioned in the previous paper [1] with the free radical diphenylpicrylhydrazyl [DPPH] has been investigated.

The relative rate of the reactions were measured colorometrically using an electrophotocolorimeter. In this case the same order in the relative reactivity of the compounds investigated was found as was established for their interaction with the *tert*butyl radical [1].

Although DPPH is stable radical, it interacts (Fig. 1a) with the compounds under consideration, and the same sequence occurs as for the reaction with the *tert*butyl radical: polyisoprene 1,4–1,4>polybutadiene 1,4–1,2>polychloroprene 1,4–4,1>polychloroprene 1,4–1,4.

At 100 and 120°C the reaction rate increases considerably (Fig. b and c.)

The reaction was also investigated in benzene solutions of different types of synthetic rubbers (Fig. 2). The order of reactivity of the rubbers is as follows: the chloroprene polymer, obtained by using diperoxide as a regulator, is the least reactive of the rubbers tested. The chloroprene polymer obtained in the presence of sulphur is more reactive, a fact apparently connected with the presence in it of polysulphide bonds [2]. The increase in reactivity of the divinyl polymer by comparison with the polyisoprene is at variance with the data obtained for the model compounds. This divergence is explained by the fact that a comparison was made of divinyl and isoprene polymers having an 86 per cent content of 1,4–1,4 units whereas the data for the divinyl models related to a compound having 1,4–1,2 units. The latter is apparently less reactive than the isoprene model having a 1,4–1,4 arrangement of units.

The data on the relative reactivity of model compounds and polymers in reactions with free radicals corresponds to the representations of their electron density. It is possible that the intramolecular co-ordination bonds formed by hydrogen in the α-methylene group with chlorine in a binary bond are responsible for the slight activity of the hydrogen atoms of α-methylene groups in the chloro-

* Vysokomol. soedin. **1**: 8, 1246–1248, 1959.

butene 1,4–1,4 units in the polymer. For polychloroprene where the arrangement of units is 1,4–4,1, such a bond is impossible. For two other model com-

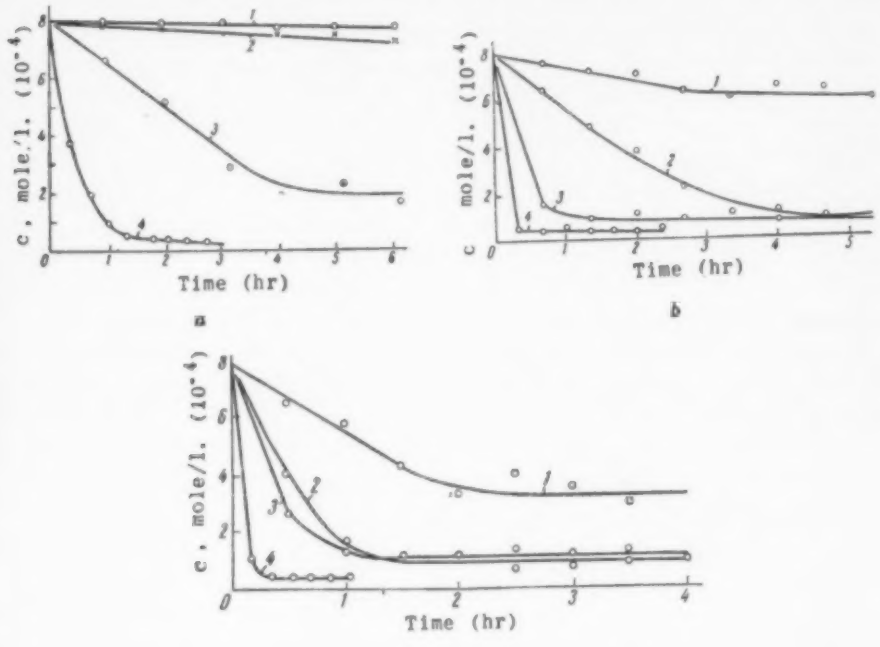

FIG. 1. The interaction of diphenylpicrylhydrazyl with model compounds: (a) at 60°; (b) at 100°; (c) at 120°. (1) 1,4–1,4 polychloroprene model; (2) 1,4–4,1 polychloroprene model; (3) 1,4–1,2 polybutadiene model; (4) 1,4–1,4 polyisoprene model.

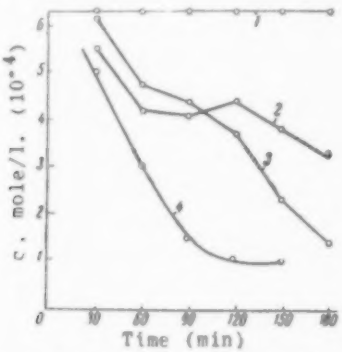

FIG. 2. The interaction of diphenylpicrylhydrazyl with rubbers at 80°. (1) polychloroprene with diproxide; (2) polychloroprene with sulphur; (3) polyisoprene (86 per cent) (1,4–1,4 units); (4) polybutadiene (85 per cent) (1,4–1,4 units).

pounds the distribution of electron density is conductive to increased mobility of hydrogen atoms in α-methylene groups.

EXPERIMENTAL SECTION

A method of synthesizing model compounds has been described in a previous paper [1]. Diphenylpicrylhydrazyl was synthesized by the methods described [3].

Tests on the interaction of DPPH with model compounds were made in 10-ml ampoules. A quantity of the corresponding compound (~0·1g) and 5 ml of a benzene solution of $8{\cdot}0\times10^{-4}$ mole l. DPPH concentration were placed in an ampoule. The ampoule was in a mixture of dry ice and acetone, blown through with nitrogen evacuated, sealed and placed in a thermostat at the appropriate constant temperature (with a variation of $\pm0{\cdot}1°$). For each compound 8–10 ampoules were taken and the time-dependence curve of the DPPH concentration was read. Measurements were made on the mark FEK-N-57 electrophotocolorimeter. Before each test a calibration curve was plotted showing the relationship of the concentration to the optical density obtained with standard solutions of DPPH from these the DPPH concentration could be determined so that the rate of change of the concentration to be found.

The rubbers themselves were purified by repeated precipitation with methyl alcohol from the benzene solution, after which they were dried in a vacuum to constant weight.

CONCLUSIONS

(1) An investigation was made of the interaction of the free radical diphenylpicrylhydrazyl with four unsaturated compounds modelling the structures of chloroprene, isoprene and divinyl polymers.

(2) The following order of reactivity of the model compounds studied was established: polyisoprene 1,4–1,4 > polybutadiene 1,4–1,2 > polychloroprene 1,4–4,1 > polychloroprene 1,4–1,4.

(3) A study was made of the interaction of the free diphenylpicrylhydrazyl radical with certain synthetic rubbers in benzene solution.

(4) Divinyl rubber having a predominant combination of units (85 per cent in the 1,4–1,4 arrangement is distinguished by its higher reactivity than the isoprene polymer having a similar 1,4–1,4 unit content (86 per cent).

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THE MECHANISM OF POLYMERIZATION IN THE PRESENCE OF THE ORGANIC COMPOUNDS OF ALKALI METALS*

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(*Received* 20 *June* 1959)

THE relationship of the structure of a polymeric chain and, correspondingly, of the properties of polymers, with the nature of the selected catalyst and medium is an interesting characteristic of the polymerization of monomers under the action of organic components of lithium, sodium and potassium. Korotkov and others [1] have shown in the polymerization of butadiene that the fraction of 1,2-structures increases on the replacement of lithium alkyl by sodium alkyl catalysts, and also on the transition from hydrocarbon to ethyl and dioxane. Tobolsky and others [2] likewise established that in the polymerization of isoprene with alkyls and aryls of alkali metals, the poly-isoprene chain structure varies with the transformation of the nature of the metal and the solvent, and is not dependent on the structure of the radical linked with the alkali metal. They also found that the styrene content in copolymers obtained on polymerization with lithium organic compounds of the styrene-butadiene [1] and styrene-isoprene systems [3] increases when the hydrocarbon solvent is replaced by ethyl. These authors show that the selective effect is determined by the polarity of the metal-carbon bond of the organo-metallic catalyst.

It is known that in the series LiR, NaR, KR, the Li-R bond is the least polar. It may be supposed that in the presence of LiR the interaction of the monomer with the catalyst will be determined both by the electron-donor properties of group R and by the acceptor properties of lithium. In the case of a typical anion mechanism (e.g. NaR in an ether medium), the growth of the chain is determined by the interaction of a monomer with a carbonian, and, correspondingly, the reactivity of a monomer is determined only by its electron-acceptor properties.

In such an examination it is to be expected that in a copolymer the content of monomers possessing the greater density of electrons in the binary bond will increase in the transition from sodium-to lithium-organic catalyst, and likewise on replacement of ethyl, amine and similar media by hydrocarbon solvents. To verify this supposition, it was essential to obtain certain quantitative data characterizing the simple sequences of these processes, and also to extend the investigation of the influence of polymerization on the composition of a copolymer

* Vysokomol. soedin. 1: No. 8, 1258–1265, 1959.

to a greater number of monomeric systems. To this end the kinetics of the simple polymerization of styrene in the presence of ethyl lithium and also the copolymerization of the butadiene-isoprene and styrene-α-methylstyrene systems with different catalysts and solvents were studied.

RESEARCH TECHNIQUES

Synthesis and purification of the starting substances. Ethyl lithium was synthesized from ethyl chloride and metallic lithium [4]. After the removal of impurities the monomers and solvents were treated with metallic sodium and twice distilled in a vacuum; purification of toluene and triethylamine was effected by treament with crystallized ethyl lithium. All the batching operations were carried out under conditions excluding moisture and air.

Kinetic measurements were made in a dilatometer equipped with a magnetic separator for the separation of the thin-walled globules with the catalyst solution. Molecular weights were determined by the viscometric method.

The composition of the copolymers was determined by the method of infrared spectroscopy by comparing the spectra of the copolymers with the spectra of mixtures of individual polymers.

RESEARCH RESULTS

Simple Polymerization. Styrene. On investigating the kinetics of simple styrene polymerization in the concentration range 0·8–2 mole/l. in the presence of ethyl lithium at a concentration of 0·001–0·011 mole/l. in benzene and toluene, and also in a mixture of toluene and triethylamine, it has been shown that the polymerization rate is proportional to the concentrations of monomer and ethyl lithium and that the molecular weight is inversely proportional to the quantity of the catalyst, and increases with increasing extent of polymerization, in accordance with data obtained by Welch [5] on the polymerization of styrene in the presence of butyl lithium in benzene and toluene. Thus, the polymerization of styrene in the presence of ethyl lithium leads to the formation of the so-called "live" polymers [6].*

It has been shown that molecular weights calculated from data on the viscosity of polymer solutions in the formula [7], $[\eta]=1{\cdot}55\times10^{-4}$, $M^{0{\cdot}74}$, coincide with the value of the molecular weights obtained from the relationship $M=(m/a)$, where m is the amount of polymerized monomer, and a, the amount of catalyst in moles (Fig. 1).

* The formation of live polymers presents an interesting peculiarity of the polymerization of monomers in the presence of organo-metallic catalysts. The circumstance leading to this is the fact that in each stage of chain growth, the nature of the active centre remains unchanged, and in the absence of mixtures disrupting the chain, the breaking reaction does not take place.

A similar relationship was observed in the polymerization of styrene in the presence of triethylamine additions. The rate of polymerization of styrene increases abruptly in the presence of a triethylamine addition (Fig. 2).

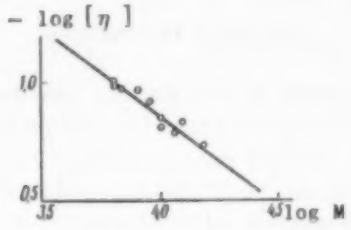


FIG. 1. The relationship between characteristic viscosity $[\eta]$ and molecular weight (M). The equation $[\eta] = 1{\cdot}55 \times 10^{-4} M^{0{\cdot}74}$ describes a straight line.

It was established that at a catalyst concentration of 0·08 mole/l., additions of triethylamine in a quantity greater than 0·16 mole/l. did not affect the polymerization rate (Fig. 3).

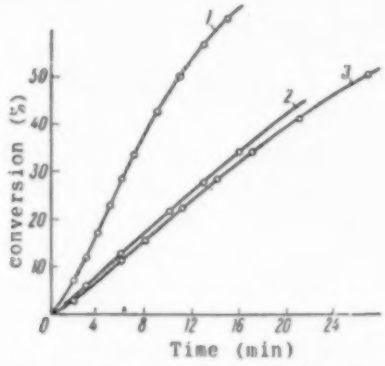


FIG. 2. The kinetics of polymerization of a 1M solution of styrene in a 0·008N solution of Li-ethyl, (1) in a mixture of toluene with a 5 per cent triethylamine solution at −18°C; (2) in toluene at 18°C; (3) in a mixture of toluene with α-methylstyrene at 18°C (α-methylstyrene concentration 1 mole/l).

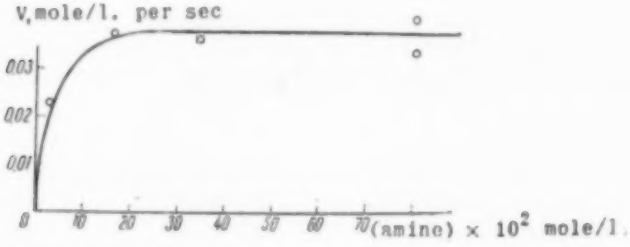


FIG. 3. The relationship between styrene polymerization rate and amine concentration at −30·8°C.

It must be noted that the polymerization rate of styrene in the presence of ethyl lithium and triethylamine is considerably lower than that of styrene in the presence of α-naphthyl sodium and small tetrahydrofuran* additions when anion polymerization is brought about in the presence of an ion pair $\overset{-}{R}\text{–}\overset{+}{Na}$: ether.

TABLE 1. THE COMPOSITION OF *iso*PRENE-BUTADIENE COPOLYMERS*

Catalyst	Yield (% by wt.)	Isoprene content in (copolymer, % by wt)
Lithium ethyl	15	29·5
Lithium ethyl	15	17·5
Triphenylmethylsodium	15	16

* Polymerization conditions for an equimolecular mixture: temperature 20°C, catalyst concentration 0·06 mole/l. on addition of 20 per cent by vol. of amine.

From the temperature relationships of the reaction rate, the activation energies E and the pre-exponential factors A, characterizing the constants of the polymerization rate of styrene in toluene in the absence and in the presence of amine additions, were determined. The relationships of log. k with $1/T$ are presented in Fig. 4a and b. In the absence of amine $E_1 = 16$ kcal/mole and $A_1 = 5 + 10^{10}$ l./mole/sec. In the presence of amine $E_2 = 13{\cdot}6$ kcal/mole and $A_2 = 6{\cdot}2 + 10^{10}$ l./mole/sec.

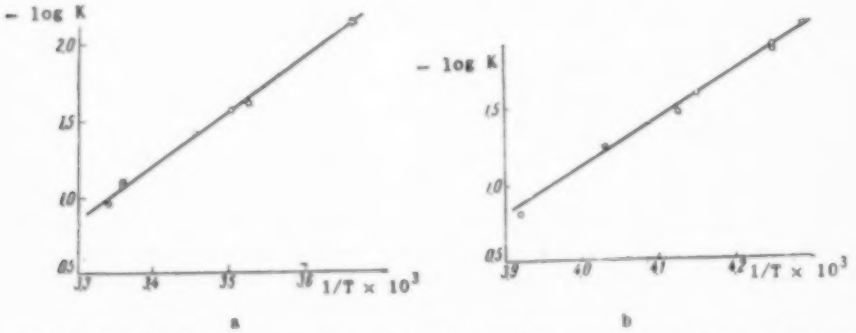


FIG. 4. Relationship between constant of velocity and temperature in the polymerization of styrene: (a) in toluene; (b) in a 0·34 M solution of triethylamine in toluene.

α-methylstyrene. In a study of the polymerization of α-methylstyrene dissolved in tetrahydrofuran (1N solution), Warsfold and Byoter [8] showed that in the presence of napthyl sodium the polymerization of α-methyl styrene no longer occurred at 25°C. The present writers have established that, in the polymerization of α-methylstyrene at monomer and catalyst concetrations of 5·6 and 1·0 mole/l.

* Data on the polymerization of styrene in the presence of α-naphthyl sodium were obtained at our Arest-Iakubovich laboratory.

respectively at 20°C, a considerable depth of transition (88 per cent) can be attained, which is linked with the upper temperature limit of α-methylstyrene polymerization at high monomer concentration [9]. The polymer obtained had the characteristic viscosity in benzene of 0·177 (mol. wt. 2900 [8].)

Copolymerization. Isoprene-butadiene. Data on the relationship of the composition of copolymers of the isoprene-butadiene system with solvent and catalyst are present in Table 1.

The styrene-α-methylstyrene system. Data on the relationship of this system with the nature of the catalyst and solvent are presented in Table 2. The present writers also studied the effect of additions of α-methylstyrene to styrene on the polymerization rate of styrene in the presence of ethyl lithium in toluene. As follows from Fig. 2, even at a methylstyrene/styrene ratio of 1:1, methylstyrene additions had no practical effect on the polymerization rate of styrene.

TABLE 2. COMPOSITION OF STYRENE-α-METHYLSTYRENE COPOLYMERS •

Catalyst	Addition	Yield (% by wt)	α-methylstyrene content in copolymer (% by wt)
Lithium ethyl	—	3	14
Lithium ethyl	—	14·4	22·5
Lithium ethyl	Sulphuric ether	14·8	8
Lithium ethyl	Triethylamine	14·5	4
Triphenylmethyl-sodium	—	10·1	6

• Conditions of polymerization: temperature 20°; catalyst concentration, 0·04 mole/l.; addition concentration, 15 per cent by vol., molecular ratio of monomers in the starting mixture: isoprene : butadiene, 1 : 1; styrene: α-methylstyrene, 1 : 5.

DISCUSSION OF RESULTS

As follows from the data obtained, according to the supposition held, the isoprene content (isoprene-butadiene system) and, correspondingly, of α-methylstyrene (α-methylstyrene-styrene system) on polymerization in the presence of ethyl lithium in a hydrocarbon medium with no additions is higher than in the presence of ethyl, amine or sodium-organic compounds. On the basis of these results the following probable mechanism of polymerization is suggested.

In the polymerization of monomers in the presence of NaR, KR, and also of LiR in an ether or amine medium, chain reaction proceeds through direct combination of the monomer with the carbanion of the catalyst

$$R\bar{M}_n\overset{+}{M}e + M \rightarrow R\bar{M}_{n+1}\overset{+}{M}e. \qquad (1)$$

However, in the case of lithium alkyls, owing to the lesser polarity of the Li-C bond, the mechanism of the polymerization differs materially from that set out above (1).

In order that the chain reactions may proceed, the Li-C bond must be polarized. In the presence of ethyl and amine additions the interaction of lithium with a pair of electrons of ethyl or amine increases the carbonian character of R in LiR and raises the reactions rate (Fig. 2). In hydrocarbon media, the monomer fulfils the role of an addition that enables the carbanion properties of R to be increased. By the method of infra-red spectroscopy [10] and a kinetic method involving the investigation of cation polymerization [11]. Terenin, Filimonov and Bystrov have shown the ability of monomers to form π-groups with Lewis' acids.

It follows from the data on cation polymerization that in their ability to form π-groups with $SnCl_4$ monomers are arranged in the following order: α-methylstyrene > isoprene > butadiene, styrene. It may be supposed that in the reactivity of monomers with lithium in lithium-organic compounds when lithium possesses the properties of Lewis' acid, they may be arranged in a similar series. The mechanism of polymerization in the presence of LiR in hydrocarbon media may be presented in the following form:

$$LiM_nR + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} M : LiM_nR \text{ (complex formation)}, \tag{2}$$

$$M : LiM_nR \xrightarrow{k_3} LiM_{n+1}R \text{ (chain growth)}. \tag{3}$$

Under the conditions of the present study, the initiation of polymerization, i.e. the transition reaction of LiC_2H_5 to $LiCHC_6H_5CH_2C_2H_5$, apparently proceeds very quickly and may influence the reaction rate only in the initial stage of the process. It should be observed that from the energy point of view the addition of monomer to the starting ethyl lithium is more favourable than the subsequent event of chain growth, and must proceed at high speed. It should also be observed that the addition of α-methylstyrene to ethyl lithium occurs in conditions where, owing to the low limiting temperature, polymerization does not take place. Thus, in a 0·85 *M* solution of α-methyl-styrene at 30°C a corresponding coloration of the solution was observed.

From the data obtained it follows that the additive reaction

$$M : LiR + M \rightarrow M : LiMR$$

either does not take place or else occurs to an insignificant degree since if it were to occur, the composition of the copolymers both in the absence and in the presence of amine additions would be identical. If also follows from data on polymerization in the presence of ethyl that the lithium in LiR compounds is a considerable weaker duplet acceptor than, for instance, $SnCl_4$, for even in the presence of relatively high ethyl concentrations not all the LiR catalyst is linked in the group with ether. Allowing that monomer is a considerably weaker duplet donor than ethyl, it may be concluded that the equilibrium concentration of the group M:LiR is small.

This supposition agrees with the fact that the addition of α-methyl-styrene, even at a 1:1 ratio with styrene, does not affect the polymerization rate of styrene since only a very small proportion of the catalyst is linked to both monomers.

The monomolecular transition reaction of a monomer complex with a catalyst in the organo-metallic compound is responsible for the chain reaction.

According to equation (3) the general chain reaction rate

$$v = \frac{k_1 k_3}{k_2 + k_4} [M][LiR],$$

where [M] is the monomer concentration, and [LiR] the lithium-organic compound concentration.

From an examination of reactions (2) and (3), it may be thought that

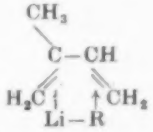
$$k_2 \gg k_3, \text{ i.e. } v = \frac{k_1 k_3}{k_2} [M][LiR].$$

This equation agrees with the proportional relationship observed between the reaction rate and the concentration of components (within the limits of the concentrations under consideration). The above mentioned peculiarities of polymerization in the presence of lithium-organic compounds clarified the causes of structural variation in the polyisoprene chain on the replacement of hydrocarbon solvents by ethyls and amines and also on the transition from lithium-organic to sodium- and potassium-organic compounds.

Tobolsky [2] has shown that polyisoprene of predominantly *cis*-form addition content is obtained on polymerization in the presence of lithium and lithium-organic compounds in hydrocarbon media. On the replacement of hydrocarbon solvents with ethyl or amine, and also of lithium-organic compounds with sodium- and potassium-organic compounds, the *cis*-form addition is lacking.

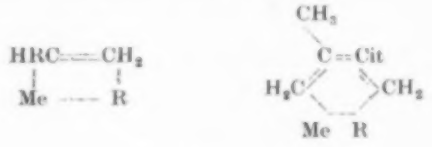
It is interesting to note that on the polymerization of isoprene by the radical [12] and cation [13, 14] mechanisms, and also under conditions of typical anion polymerization (NaR+ethyl) [2] polyisoprene of a predominantly 1-4-*trans*-form addition content is obtained. It may be assumed that the minimum activation energy corresponds to this type of addition in all three mechanisms. This assumption is supported by data obtained on the radical polymerization of isoprene [12] in which the proportion of the *cis*-structure grows with increase in temperature.

In the presence of LiR the binary bond of isoprene occurring in the 1–2 state and possessing a higher election density will interact favourably with the lithium component of the catalyst, in consequence of which the following *cis*-form addition will be the most favourable spatial arrangement:



Thus, the chain reaction in these systems is determined not only by the ability of monomer to form carbonian, but also by its ability to interact with the lithium component of the catalyst.

Apart from the above diagram of polymerization with the two-phase progress of chain reaction, the diagram, according to which the chain reaction occurs as a single primary process, also seems effective. In this case the reaction occurs through the introduction of monomer having a metal-carbon bond, and the transitional state occurs as a four-period cycle in the polymerization of defines and as a six-period cycle in the polymerization of dienes:



This diagram agrees completely with all the experimental relationships found, and, as with the first diagram, explains the above-mentioned peculiarities of the structure of the polymeric chain under the action of LiR (by comparison with other organo-metallic compounds), since it also postulates the participation of the lithium component of the catalyst, which possesses the properties of Lewis' acid, in the chain reaction.

Further investigations are necessary to solve the question as to which of the two proposed diagrams takes place.

It is noted in conclusion that the data obtained on the constitutions of copolymers and the corresponding constants of copolymerization in polymerization under the action of lithium-organic catalysts in hydrocarbon media, is not characteristic of the reactivity of monomers in relation to the corresponding carbanions.

In order to obtain data on relative reactivity in a typical anion mechanisms of polymerization it is necessary to investigate copolymerization in the presence of sodium-, potassium-, or lithium-organic compounds and of additions having strong electron-donor properties.

The authors express their gratitude to T. V. Talalayeva for her assistance in the synthesis of the ethyl lithium.

CONCLUSIONS

(1) In the polymerization of styrene in the presence of ethyl lithium in benzene or toluene both with and without additions of triethylamine, the polymerization rate in the range of concentrations studied is proportional to the ethyl lithium and monomer concentrations.

(2) The average degree of polymerization is determined by the relationship:

$$\text{molecular weight} = \frac{\text{amount of polymerized monomer}}{\text{amount of catalyst}}.$$

(3) A decrease of 2·4 *kcal* ($E_1 = 16$ kcal, $E_2 = 13{\cdot}6$ kcal) in the activation energy of the reaction of styrene polymerization in the presence of ethyl lithium leads

to higher polymerization rates in the presence of triethylamine additions. The pre-exponential factors in both cases are correspondingly close and equal:

$$A_1 = 5 \times 10^{10} \text{ l./mole/sec}$$

and

$$A_2 = 6 \cdot 2 \times 10^{10} \text{ l./mole/sec}$$

(4) The higher content of isoprene and α-methylstyrene in copolymers of the isoprene-butadiene and α-methylstyrene-styrene systems in polymerization in the presence of ethyl lithium in hydrocarbon media, by comparison with the composition of copolymers obtained in the presence of amine or ether additions, and also in the presence of sodium-organic compounds, is explained by the participation not only of a carbanionic but also of a lithium constituent catalyst in the chain reaction.

Translated by D. K. BROOKS

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SYNTHESIS OF POLYMETHYL METHACRYLATE WITH REGULAR MICROSTRUCTURE*

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(*Received* 4 *May* 1959)

THE present investigation was proposed starting from the hypothesis that four- or six-membered rings must be formed in an intermediate stage in the homogeneous catalytic polymerization of methyl methacrylate (MMA). In this case, the polymer must possess a regular microstructure † and be different in behaviour from the polymethyl methacrylate (PMMA) obtained by a radical chain mechanism. In fact, the PMMA obtained by us at −50–80° possessed the following mew properties: (1) the softening temperature was about 50° lower than for ordinary PMMA; (2) the specific gravity was 1·230, as compared with 1·205; (3) the dielectric losses at the glass temperature possessed a considerably higher maximum (Fig. 1); (4) the breadth of the resonance line (ΔH), measured by the method of nuclear magnetic resonance, undergoes a sharp reduction in the neighbourhood of the softening temperature (50–60°) for catalytic PMMA, while with ordinary PMMA, a gradual narrowing of the resonance line is observed in the glass state of the polymer and a sharp reduction takes place only in a region of temperature considerably lower than the softening temperature (Fig. 2).

Our attempts to obtain a sample of PMMA possessing a clearly defined crystalline structure were unsuccessful. Fox *et al.* [2,3], have shown that crystallizable PMMA can be obtained in three configurations: isotactic (type II), syndiotactic (type I) * and a block polymer of these structures (type III). Isotactic PMMA was obtained by these authors under conditions similar to ours, i.e. in toluene at −60° in the presence of fluorenyl-lithium.

It was of interest to investigate the reason for the divergence of the results. It appeared that PMMA precipitated with methyl alcohol, as produced by us earlier, cannot be crystallized by the method usually used–prolonged standing in the swollen state in a suitable solvent ("tempering" of the polymer). If, how-

* Vysokomol. soedin. 1: No. 9, 1319–1326, 1959.

† For a short account of the polymerization of MMA with butyl-lithium, see [1].

* In the paper of Fox, Good *et al.* [2], isotactic PMMA is erroneously characterized as syndiotactic, and the syndiotactic variety as isotactic (see [3]).

ever, PMMA is precipitated with, for example, *n*-hexane, then the polymer obtained crystallizes by the "tempering" method; crystallinity can be detected by the usual method of X-ray analysis.

If a sample of PMMA which possesses a crystalline structure after "tempering" (in our case, the two samples had softening temperatures of 62 and 67°) is dissolved in toluene and precipitated with methanol, then a specimen with a new softening temperature (in our case 74 and 83°), which is no longer crystallizable is obtained.

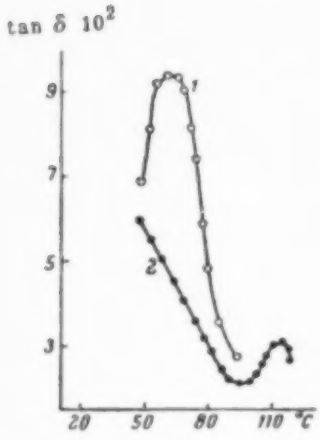


FIG. 1. Dielectric losses of PMMA: (1) Isotactic; (2) Atactic.

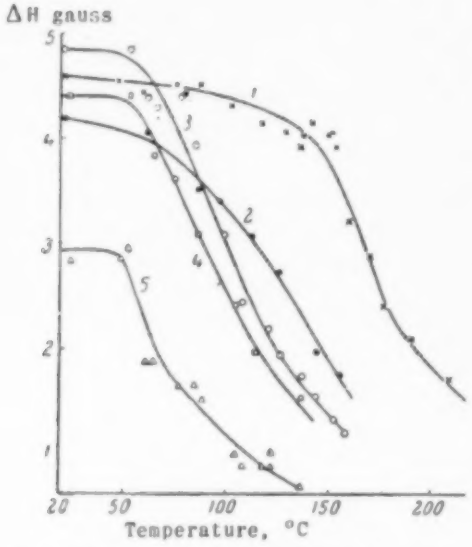


FIG. 2. Variation in the breadth of the resonance lines of specimens of PMMA with temperature. (1) Radical-polymerized PMMA, T_g (glass temperature) = 105–115°; (2) Radical-polymerized technical, T_g = 105–114°; (3) Catalytic PMMA; T_g = 74°; (4) Do., T_g = 46°.

Further, if a solution of PMMA is prepared in water and is then precipitated with hexane, or if a sample of PMMA precipitated from a toluene solution with hexane and existing in the swollen state is treated with water and the solvent is then removed, a polymer incapable of crystallizing is again obtained.

We explain this interesting phenomenon in the following way: methanol and water, being capable of forming hydrogen bonds, react with the carbonyl groups of the polymer and by that very fact "screen" their ordering properties. Such "screening" interferes with the capacity of the macromolecules for mutual orientation and the precipitated polymer, therefore, not being orientated, cannot crystallize on "tempering". By using a solvent incapable of forming hydrogen

bonds (e.g. toluene), the precipitated polymer, in consequence of the mutual orientation of the macromolecules, contains orientated macromolecular clusters and, consequently, is capable of crystallization [8].

EXPERIMENTAL PART

Methyl methacrylate was freed from stabilizer by treatment with a 4% solution of sodium carbonate, washed with water, dried over calcium chloride and sodium wire and distilled through a fractionating column. *Toluene*, *hexane* and *diethyl ether* were purified by the usual methods and stored over sodium wire. Pyridine was boiled with solid alkali and distilled; before use it was subjected to a supplementary distillation over sodium wire. *Liquid ammonia*, carefully dried, was condensed into a storage vessel to which sodium wire had been added. The ammonia was distilled into the reaction flask from the storage vessel.

Butyl-lithium was prepared in hexane by Gilman's method [4]; *triphenylmethyl-lithium*, in ether, the ether being subsequently distilled off and toluene added; and *fluorenyl-lithium* in hexane by the interaction of an excess of *n*-butyl-lithium and fluorene [6]. The precipitate of fluorenyl-lithium was washed with hexane 3–4 times by decantation and the solvent (toluene) added.

Ethylene glycol dimethyl ether was obtained by the reaction of ethylene glycol with dimethyl sulphate [7].

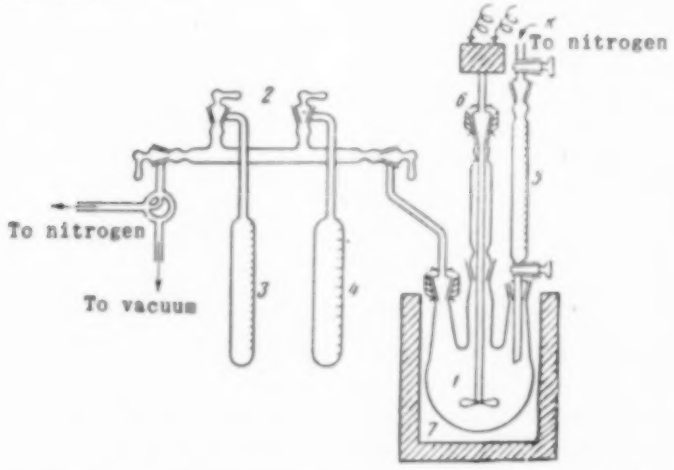


FIG. 3. Sketch of the polymerization apparatus. Reaction flask; (2) Distributing manifold; (3) (4) (5) Measuring vessels; (6) Stirrer; (7) Cryostat.

All operations were carried out under vacuum or in an atmosphere of technical nitrogen freed from traces of oxygen and moisture.

A sketch of the apparatus for preparing crystallizable PMMA is given in Fig. 3.

The reaction flask and measuring vessels for the monomer, the solvent and the catalyst were given a preliminary heating under vacuum at 250–300°. The polymerization was carried out in an atmosphere of nitrogen with a cryostat temperature of −50, −60°. The concentrations of monomer and catalyst amounted to 1 g/l. and 0·03–0·05 g/l., respectively. The polymer was precipitated from solution with hexane and dried in the thermostat. In some special experiments, the polymer was precipitated with methanol and washed free from alkali with water. The polymer prepared in liquid ammonia was removed from the flask after the ammonia had been distilled off and immediately dried in the thermostat.

The results of the principal experiments are given in Table 1.

TABLE 1. PROPERTIES OF CRYSTALLIZABLE PMMA OBTAINED AT A TEMPERATURE OF −60 TO −50°C

Solvent	Catalyst	Time (hr)	Yield (%)	Vicat softening temperature	[η]
Toluene	Butyl-lithium	0·75	90	52	1·02
,,	Fluorenyl-lithium	0·75	90	50	0·96
,,	Trityl-lithium	1·50	60	53	1·68
Hexane	Butyl-lithium	47	72	57	0·6
Diethyl ether	,, ,,	24	88	80	0·5
Ethylene glycol Dimethyl ether	,, ,,	0·75	71	92	—
Pyridine	,, ,,	3	55	135	—
Liquid ammonia	,, ,,	24	23	135	—
None	Benzoyl peroxide	45	99	110	—

DISCUSSION OF THE EXPERIMENTAL RESULTS

In the polymerization of MMA at −60° in toluene with butyl-lithium, fluorenyl-lithium and triphenylmethyl-lithium, crystallizable polymers with a similar softening temperature are obtained in good yield. All three specimens of PMMA possess similar infra-red spectra, different from the spectrum of radical-polymerized methyl methacrylate (Fig. 4).

The three samples of PMMA obtained, after swelling in heptan-4-one for 16 hr and drying, gave similar Debye diagrams. The microphotometric curve of the Debye diagram for one specimen, prepared in the presence of butyl-lithium, is given as curve 2 (Fig. 5).

In the absence of the preliminary treatment in hexan-4-one or another suitable solvent (for example, methyl ethyl ketone), these specimens give the X-ray diagram of an amorphous polymer. Comparison of the results of the infra-red spectra, the Debye diagrams and the softening temperatures of the specimens of PMMA obtained by the polymerization of MMA in toluene with butyl-lithium,

fluorenyl-lithium and triphenylmethyl-lithium shows their indentity with the PMMA having the isotactic structure (type II) described in the work of Fox and Stroupe [2,3].

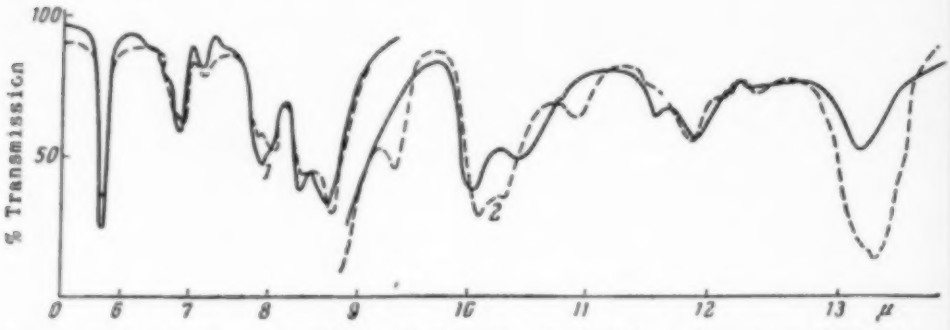


FIG. 4. Infra-red spectra of PMMA. (1) Isotactic, obtained by polymerizing MMA with organolithium compounds. (2) Atactic, polymerization of MMA with benzoyl peroxide.

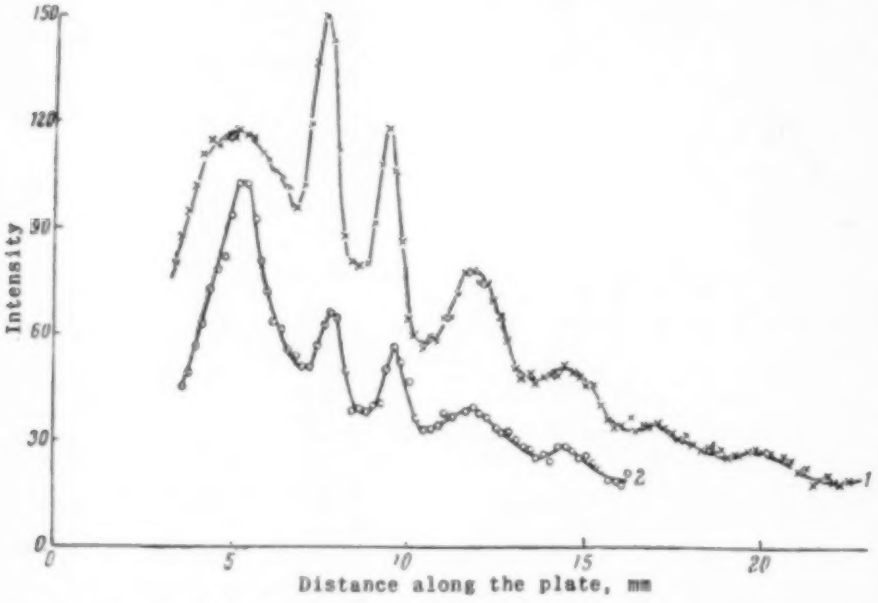


FIG. 5. Microphotometric curves of the Debye diagrams of isotactic and syndiotactic PMMA. Cu K_α radiation. (1) Syndiotactic; (2) Isotactic.

In the case of polymerization in hexane, the PMMA separates out as a fine precipitate. The velocity of the process in this case is considerably less than in toluene (Table 1). The structure of the PMMA obtained, from its infra-red spectrum and its softening temperature, corresponds to isotactic PMMA.

On replacing toluene with a more strongly solvating solvent (for example, liquid ammonia or pyridine), we obtained polymers with a decreased specific gravity (1·18 instead of 1·23 for the isotactic and 1·25 for the atactic form) and a softening temperature of 135° instead of 50–60° (Table 1).

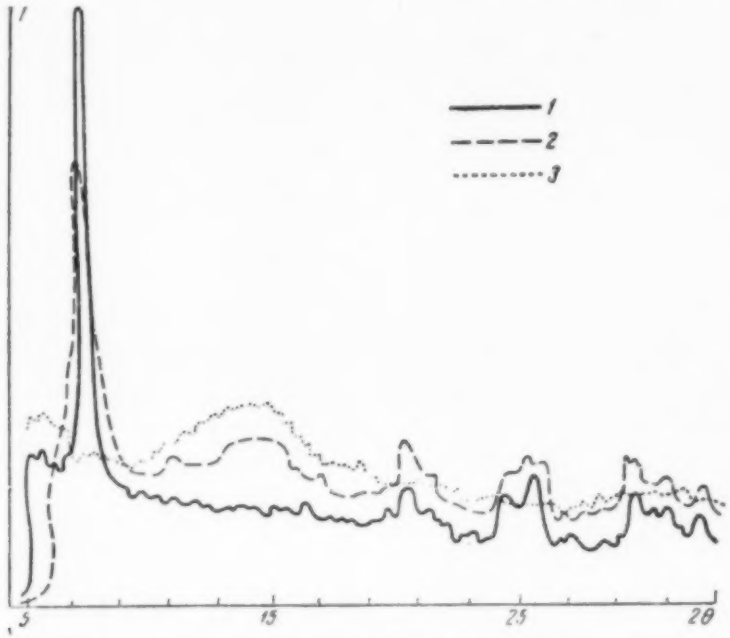


FIG. 6. X-ray diagrams of some samples of PMMA, obtained with an ionization apparatus. (1) Syndiotactic, in pyridine; (2) In ethylene glycol dimethyl ether; (3) Atactic.

After "tempering" in heptan-4-one, a clear X-ray diagram of the crystalline form was obtained for these polymers (Fig. 6) *. The infra-red spectra of these polymers coincide with the spectrum of isotactic PMMA. The polymers obtained are identical in structure with the specimens of syndiotactic PMMA (type I) described by Fox *et al.*

The microphotometric curve of the Debye diagram for syndiotactic PMMA is given in Fig. 5, 1.

The interplanar distances (d) for isotactic and syndiotactic PMMA (disagreement only at $d = 6{\cdot}46$ Å) are given in Table 2. For the isotactic polymer a distinct peak exists in the region of 6·46 Å, while for the syndiotactic polymer there is an amorphous halo in this region.

* The X-ray spectroscopic investigation was carried out by recording the scattered radiation with a Geiger counter.

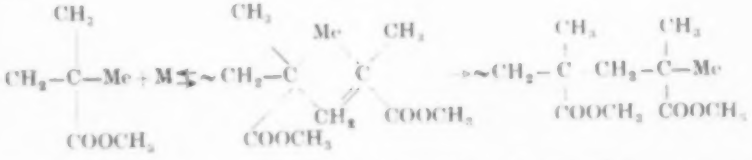
The polymer formed in ethylene glycol dimethyl ether possesses a less distinct syndiotactic structure (Fig. 6). Its softening temperature is also somewhat lower (96°) than for the polymer formed in pyridine or liquid ammonia. The polymer formed in diethyl ether, on the other hand, possesses an infra-red spectrum identical with the spectrum of isotactic PMMA. Nevertheless, its softening

TABLE 2. INTERPLANAR DISTANCES *D* IN Å FOR PMMA OF ISOTACTIC AND SYNDIOTACTIC STRUCTURE

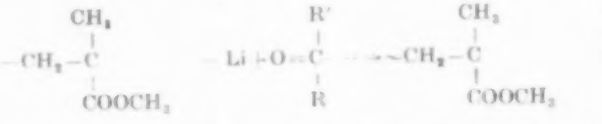
Isotactic PMMA	Syndiotactic PMMA
6·46	Amorphous
4·42	4·52
3·66	3·74
3·08	3·08
2·64	2·63

temperature (80°) is considerably higher than for isotactic PMMA (Table 1). It can be assumed that the PMMA formed in these ethers possesses isotactic and syndiotactic blocks in different proportions. Apparently, in the case of the ethylene glycol ether blocks of type (I) predominate, and in the case of diethyl ether those of type (II).

This importance of the effect of the nature of the solvent on the course of the MMA polymerization reaction can be explained in the following way. Where the polymerization takes place in solution in hydrocarbons not forming a complex with the organolithium compound and, consequently, not solvating it, it is possible to imagine the course of the reaction as an organometallic synthesis or as taking place through the formation of a very weak complex possessing a high reactivity. In the case where the reaction takes place as an organometallic synthesis:



Chain-breaking reactions as a result of the action of a reaction centre on a C=O linkage of the monomer or polymer must play an essential role:



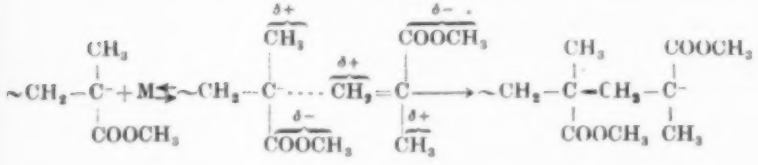
It is therefore difficult to anticipate the formation of a high molecular polymer even when the reaction is carried out at low temperatures.

The other reaction mechanism is more probable: a weak complex between the end group of the growing polymer chain and the monomer forms an active centre. The chain-building reaction consists in the retention of the configuration of the active complex at the end of the growing chain after the addition of this molecule of monomer.

The question will be examined in detail in subsequent communications on the mechanism of the action of solvating additives and solvents on the kinetics of the polymerization of methyl methacrylate, divinyl and styrene and the copolymerization reactions *. Here, it is important to note that, in polymerization in hydrocarbon solutions, four- and six-membered rings of strictly determined structure are formed in the transitional stage. As a result, the monomer molecules always add on to the end of the growing polymer chain in a unique arrangement, which leads to the formation of the isotactic polymer in the case of the polymerization of methyl methacrylate and to 1,4 polymer structures in the case of isoprene and divinyl.

If the solvent is one which solvates organolithium compounds, the active centre will be a dipole on which the directing action of the cation is weakened or, in the limiting case, a carbanion. The transitional state will therefore possess a linear structure and the course of the addition of the monomer molecules to the growing polymer chain will be determined by the distribution of electric charges on the reacting molecules, since the reaction takes place between weakly polarized molecules or ions and induced dipoles. For example, in the limiting case the course of the reaction may be represented by the following scheme:

$$RLi + C \leftrightarrows \overset{\delta+}{R}-Li \ldots C \leftrightarrows R^- + [LiC]^+$$



With the linear structure of the transitional state, similar substituents in the monomer and polymer molecules will tend to occupy remote positions, which necessarily leads to the formation of a polymer of the syndiotactic structure. Since solvation of the organolithium compounds or the active centres of polymerization is an equilibrium reaction and the duration of the elementary chain-building reaction can exceed by several times the time of existence of the solvated or unsolvated molecule, favourable conditions are established for the formation of peculiar block polymers.

By varying the nature of the solvent (with respect to the stability of the solvators), the concentration of the solvating agent and the temperature, it is

* For a short account, see [9].

possible to select conditions under which one and the same growing molecule will react in the solvated stage, forming a "syndiotactic block", and then in the unsolvated state, giving an "isotactic block", then again in the solvated state, again in the unsolvated state and so on.

In the light of these ideas, of the ethers investigated by us, diethyl ether gives the least stable solvates with organolithium compounds and ethylene glycol dimethyl ether occupies an intermediate position between diethyl ether and pyridine or liquid ammonia.

The infra-red spectroscopic investigation was carried out by V. A. Nikitin and N. V. Mikhailova. The dielectric losses were studied by G. P. Mikhailov and T. I. Borisova. The investigation of the nuclear magnetic resonance of the polymers was carried out by N. M. Bazhenov, M. V. Bol'kenshteino, A. M. Kol'tsov and A. S. Khachaturov. We take this opportunity to express our thanks to these colleagues.

CONCLUSIONS

(1) In the catalytic homogeneous polymerization of methyl methacrylate with butyl-lithium or other organolithium compounds, polymers of regular microstructure are obtained. The nature of the medium affects the stereospecificity of the polymer: in the case of a weakly solvating solvent, such as toluene or hexane, isotactic PMMA is obtained; if strongly solvating solvents (liquid ammonia, pyridine) are used, syndiotactic PMMA is obtained; and if solvents with a medium solvating power (diethyl ether and ethylene glycol methyl ether), block polymers of these two configurations in various proportions are obtained.

(2) The radical of the initial organolithium compound has no influence on the stereospecificity of the polymer.

(3) The nature of the precipitant has an essential influence on the capacity of the PMMA to crystallize on "tempering".

(4) Precipitation of the polymer with methanol or previous treatment of it with water adversely affects its power to crystallize.

Translated by B. J. HAZZARD

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CHARACTERISTICS OF THE MECHANISM OF CATIONIC POLYMERIZATION—I. COPOLYMERIZATION OF THE SYSTEMS α-METHYLSTYRENE-STYRENE, *ISO*BUTYLENE-STYRENE AND VINYL *n*-BUTYL ETHER-STYRENE*

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(*Received* 1 *June* 1959)

At the present time a considerable number of investigations has been devoted to the study of the kinetics of the cationic polymerization of unsaturated compounds. However, in the majority of investigations the possibility of the formation of π-complexes of the catalyst with the monomer and their influence on the initiation of polymerization is not taken into account in investigating the process.

Combination of the investigation of the kinetics of separate polymerization and copolymerization for a series of monomers has made it possible for us to discover a series of new kinetic effects which cannot easily be explained without allowance for the effect of complex formation between the catalyst and the monomer.

TABLE 1. COMPOSITIONS OF THE COPOLYMERS FROM THE STYRENE-α-METHYLSTYRENE SYSTEM

Experiment No.	Content of α-methylstyrene, (moles %)		Yield of copolymer (%)
	In the initial monomer mixture	In the copolymer	
89	4·4	15·8	5·9
16	8·5	36·1	2·3
14	18·9	57·1	12·9
10	47·7	77·0	20·3
1	57·2	83·3	9·2
17	68·1	83·6	27·3

The present work is devoted to the investigation of the cationic copolymerization of the three systems: styrene-α-methylstyrene; styrene-*iso*butylene;

* Vysokomol. soedin. **1**: No. 9, 1333–1341, 1959.

and styrene-vinyl butyl ether. The kinetics of the copolymerization of these systems in ethyl chloride in the presence of stannic chloride as catalyst was investigated and the compositions and molecular weights of the copolymers obtained were determined. The kinetics of copolymerization were determined by means of a dilatometric method, as described earlier [1]. The compositions of the copolymers were determined by infra-red spectroscopy by comparing the spectra of the copolymers with the spectra of mixtures of the separate polymers. Fifteen per cent solutions of the polymers in carbon tetrachloride were used for the exposures. The molecular weights of the copolymers were found by an osmotic method, methyl ethyl ketone being used as the solvent.

Styrene-α-methylstyrene system. The compositions of the copolymers are given in Table 1.

As can be seen from Table 1, the compositions of the copolymers are greatly enriched in the more active component -α—methylstyrene, the enrichment being considerably greater in the region of a small initial content of α-methylstyrene. On the basis of the results for the compositions found, the calculated constants for the copolymerization were $\alpha = 0{\cdot}05$ (styrene) and $\beta = 2{\cdot}90$ (α-methylstyrene).

The molecular weights of the copolymers are given in Table 2.

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TABLE 2. MOLECULAR WEIGHTS OF THE COPOLYMERS

Experiment No.	Initial molar ratio of styrene to α-methylstyrene	Molecular weight	Yield of polymer (%)
94	1:0	70·000	—
67	22·5:1	54·900	58·6
63	11·3:1	47·000	73·0
89	21·5:1	28·200	5·9
27	4·5:1	23·800	24·7
23	1·10:1	26·400	22·0
31	0·47:1	21·400	27·4
28	0·28:1	23·500	19·0
54	0:1	26·700	50·2

The velocities of copolymerization in the region of molecular ratios of the components from 1 : 4 to 4 : 1 are characterized by the series of curves shown in Fig. 1. The copolymerization process takes place without an induction period with gradually decreasing velocity. The kinetic picture changes sharply, however, on moving to a region of small concentrations of α-methylstyrene (Fig. 2). The initial velocity of polymerization in this case is reduced in comparison with the velocity of the separate polymerization of styrene. In Fig. 3 is shown the dependence of the initial velocity of polymerization on the initial ratio

of the monomers. The reduction of the velocity in the region of small concentrations of α-methylstyrene (minimum of the curve) corresponds to a decrease

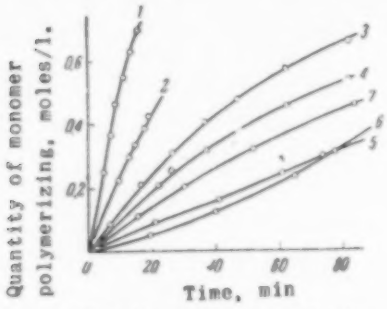

FIG. 1. Velocity of copolymerization for the styrene-α-methylstyrene system $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers, 2,5 moles/l.; temperature, 0°. Initial molar ratio of styrene-α-methylstyrene: (1) 0:1; (2) 1:4; (3) 1:2·5; (4) 1:1; (5) 2·5:1; (6) 4:1; (7) 1:0.

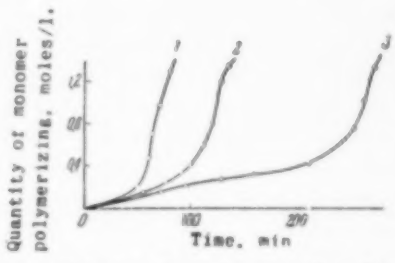

FIG. 2. Velocity of copolymerization for the styrene-α-methylstyrene system at low concentrations of α-methylstyrene $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers 2,5 moles/l.; 0°. Initial molar ratio of styrene to α-methylstyrene: (1) 26:1; (2) 49:1; (3) 124:1.

in the molecular weight (Table 2, experiments 94 and 89) and is connected, consequently, with a decrease in the velocity of chain building.

On the whole, the polymerization curves in the region of a small content of α-methylstyrene have an appearance characteristic of non-stationary processess. After a certain induction period, there follows a sharp increase in the velocity of polymerization with time. In this the velocity increases to 10 times the velocity of the separate polymerization of styrene.

Comparison of the mean degree of polymerization of the polymers obtained during the initial acceleration with the mean degree of polymerization of polystyrene obtained without the acceleration under the same conditions (Table 2, experiments 63, 67 and 94) shows that the effect of the acceleration of the velocity of polymerization with time is not associated with an increase in the molecular weight and is dependent on an increase in the velocity of initiation. The results of experiments on the influence of small quantities of H_2O and HCl on the acceleration effect are in conformity with this conclusion.

As can be seen from Fig. 4, the addition of these substances in quantities commensurate with the concentration of the catalyst destroys the acceleration effect completely or to a considerable extent. It is known that H_2O and HCl molecules readily give complexes with Friedel-Crafts catalysts. In binding the catalyst into a complex, they must by that very fact alter the conditions of initiation and, consequently, influence all the processes connected with actions of initiation. Hence, their influence on the increase in velocity with time in the given case is in agreement with the conclusion that this increase is dependent on actions of initiation.

The S-shaped form of the kinetic curves indicates that, in the initial stage of the process, an accumulation takes place of formations more active than those which can be present in the separate polymerization of styrene under

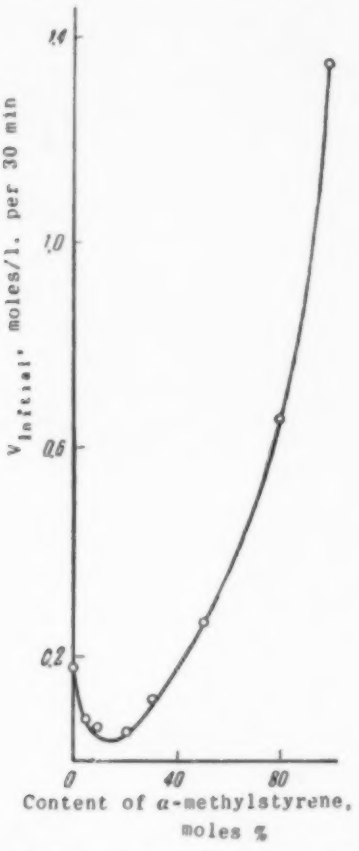

FIG. 3. Dependence fo the initial velocity of polymerization on the composition for the styrene-α-methylstyrene system $[SnCl_4]=0{\cdot}002$ moles/l. Total concentration of monomers, 2·5 moles/l.; temperature 0°C.

the same conditions. The observed induction period may represent a characteristic of the velocity of this accumulation. The dependence of the induction period on the initial concentration of the components was investigated.

Fig. 5 and 6 show that the induction period is inversely proportional to the concentrations of α-methylstyrene and $SnCl_4$. The induction period does not depend on the initial concentration of styrene.

Thus:

$$\frac{1}{\tau} = k\,[SnCl_4]\cdot[\alpha\text{-methylstyrene}].$$

Carrying out the polymerization of the system investigated over a wide range of temperatures (from −78 to 35°) showed a very strong dependence

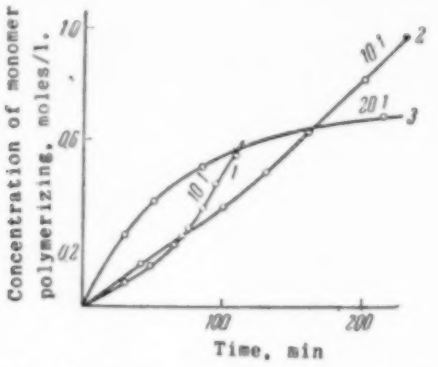

FIG. 4. Influence of the addition of H_2O and HCl on the acceleration effect. Total concentration of monomers, 2·5 moles/l.; 0° (1) 0·002 moles/l. $SnCl_4$, 0·004 moles/l. HCl; (2) 0·002 moles/l. $SnCl_4$, 0·010 moles/l. HCl; (3) 0·006 $SnCl_4$, 0·012 moles/l. H_2O. The figures on the curves show the molar ratio of styrene to α-methylstyrene.

of the acceleration effect on the temperature, while both the induction period and the magnitude of the maximum velocity also proved to be strongly temperature-dependent.

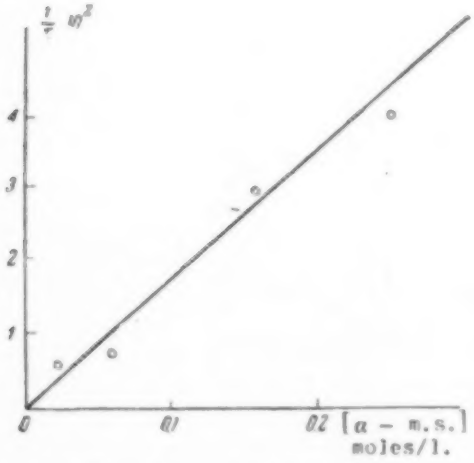

FIG. 5. Dependence of the induction period on the concentration of α-methylstyrene [$SnCl_4$] = 0·002 moles/l. Total concentration of monomers, 2·5 moles/l.; 0°.

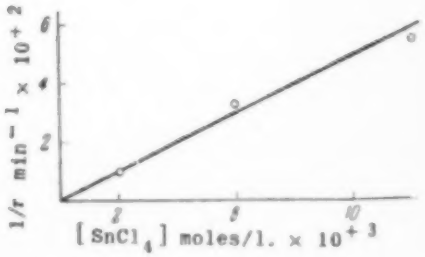

FIG. 6. Dependence of the induction period on the concentration of $SnCl_4$. Total concentration of monomers, 2·5 moles/l. Initial molar ratio of styrene to α-methylstyrene, 20:1; 0°.

The course of the polymerization curves at various temperatures is shown in Fig. 7.

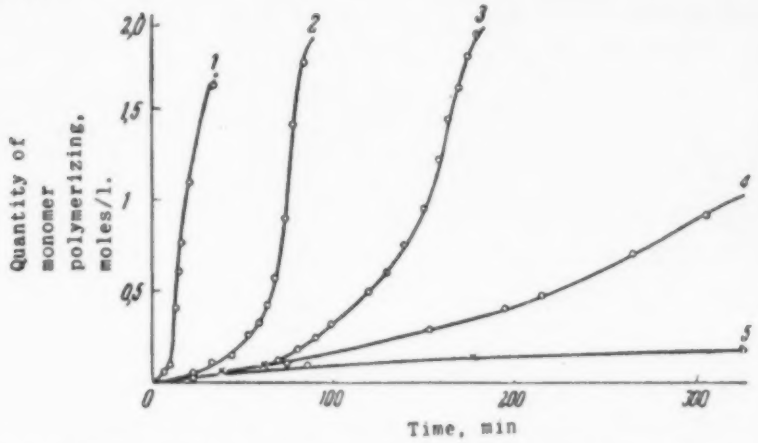

FIG. 7. Dependence of the increase in the polymerization velocity effect on the temperature. $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers, 2·5 moles/l. Initial molar ratio of styrene to α-methylstyrene, 20:1; (1) 20°; (2) 10°; (3) −20°; (4) −30°; (5) −78°.

In Fig. 8 is given the dependence between $\ln 1/\tau$ and $1/T$, which leads to the value of the activation energy of the reaction, 7·8 kcal/mole.

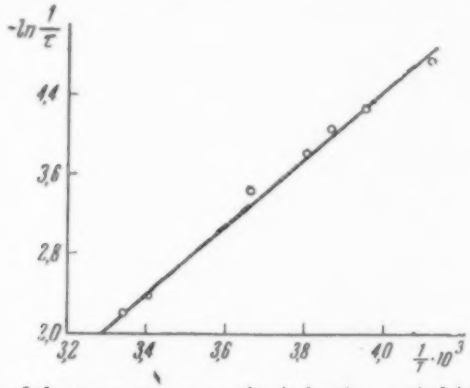

FIG. 8. Influence of the temperature on the induction period in the styrene-α-methylstyrene system. $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers, 2·5 moles/l. Initial molar ratio of styrene to α-methylstyrene, 20:1; 0°.

The dielectric constant of the medium and the nature of the solvent exert great influence on the magnitude of the effect under consideration.

In Fig. 9 is shown the course of the polymerization process for the system considered in four solvents–ethyl chloride, dichloroethane, carbon tetrachloride and benzene at 0°. As can be seen from Fig. 9, the induction period of the process

in dichloroethane is very much less than in ethyl chloride, and in such weakly polar solvents as CCl_4 and benzene the acceleration could not be observed even when the course of the process was greatly prolonged (at 0°).

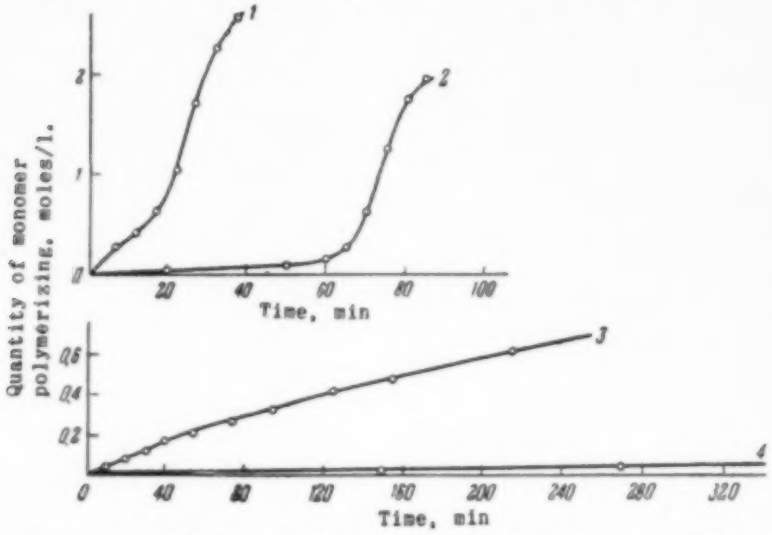

FIG. 9. Influence of the nature of the solvent on the acceleration effect at 0°. (1) 1·2-dichloroethane; (2) ethyl chloride; (3) benzene; (4) carbon tetrachloride. $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers, 2·5 moles/l. Initial molar ratio of styrene to α-methylstyrene, 20:1; 0°.

In the polymerization of the system studied in CCl_4, the process was begun almost immediately after the polymers were mixed, even if with only a very small velocity, whereas in the separate polymerization of styrene it takes place with a long period of complete absence of polymerization (1·5 hr at 0°). α-Methylstyrene under the same conditions shows almost no such period (Fig. 10).

Styrene-isobutylene system. The compositions of the copolymers for the above system are given in Table 3.

TABLE 3. COMPOSITION OF THE COPOLYMERS FOR THE STYRENE-*iso*BUTYLENE SYSTEM

*Iso*butylene content (moles %)		Yield of copolymer (%)
In the initial monomer mixture	In the polymer	
45·7	63·7	28
60·8	73·7	21
78·1	84·1	31
26·8	54·1	21
19·8	37·1	10

The copolymers are enriched in the more active component—*iso*butylene, while, as in the styrene -α-methylstyrene system, the enrichment is greater the smaller the initial content of the more active monomer.

On the basis of the data for the compositions of the copolymers, the copolymerization constants were calculated as $\alpha_1 = 0{\cdot}17$ (styrene) and $\beta_1 = 1{\cdot}6$ (*iso*butylene).

In the determination of the compositions of the copolymers by infra-red spectroscopy it was discovered that, while the copolymers are readily soluble in CCl_4, mixtures of the separate polymers of the same composition form systems in various solvents (CCl_4, $C_2H_4Cl_2$, CS_2, etc.) separating into layers, as a result of which, in taking the spectra for the calibration curve, micro-inhomogeneities were always observed, appearing in the form of turbidity of the solution. Therefore, for checking the results obtained for the compositions, copolymers of *iso*butylene and *p*-chlorostyrene were prepared. The compositions of the copolymers of this system are given in Table 4.

TABLE 4. COMPOSITION OF THE COPOLYMERS FOR THE *iso*BUTYLENE-*P*-CHLOROSTYRENE SYSTEM

*Iso*butylene content (moles %)		Yield of copolymer (%)
In the initial monomer mixture	In the copolymer	
20·1	50·5	22
29·2	64·7	23
33·8	62·3	11
42·0	72·4	10

The copolymerization constants calculated on the basis of these results—$\alpha_2 = 0{\cdot}05$ (*p*-chlorostyrene) and $\beta_2 = 2{\cdot}90$ (*iso*butylene)—make it possible to check the accuracy of the results obtained by comparing them with the results given in the literature.

According to the results of Overberger and coworkers [2] for the styrene-*p*-chlorostyrene system, $\alpha_3 = 2{\cdot}5$ (styrene) and $\beta_3 = 0{\cdot}30$ (*p*-chlorostyrene). Assuming that the relationship between the reactivity of styrene (st.) and *iso*butylene (is.) in respect of the carbonium ion of styrene and *p*-chlorostyrene (*p*-chl.) has the same value, we obtain the following value for constant α_1:

$$\alpha_1 = \frac{k_{\text{st. st.}}}{k_{\text{st. is.}}} = \frac{k_{p-\text{chl. st.}}}{k_{p-\text{chl. is.}}} = \frac{\alpha_3}{\beta_3} = 0{\cdot}17,$$

which agrees with the value of α_1 given above, obtained by us from the spectroscopic data.

The velocity of copolymerization of styrene and *iso*butylene as a function of the composition of the starting mixture, at 0°, is shown in Fig. 11.

As can be seen from the Figure, here, just as with the styrene-α-methylstyrene system, a higher velocity of polymerization is observed in the region of a smaller initial content of the more active monomer. However, the region where this effect is displayed is shifted, in comparison with the styrene-α-methyl-

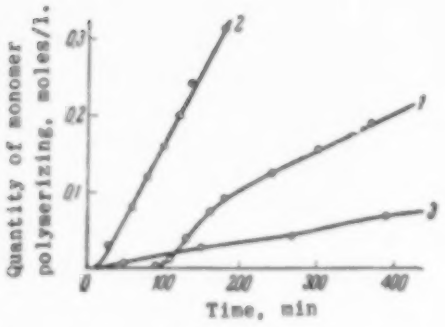

Fig. 10. Velocity of polymerization in CCl_4 at 0°. (1) 0·055 moles/l. $SnCl_4$; 2·5 moles/l. styrene; (2) 0·006 moles/l. $SnCl_4$, 2·5 moles/l. α-methylstyrene; (3) 0,055 moles/l. $SnCl_4$, 2·3 moles/l. styrene and 0·12 moles/l. α-methylstyrene.

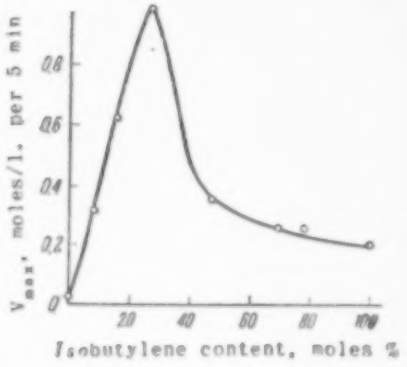

Fig. 11. Dependence of the maximum velocity on the composition of the starting mixture for the styrene-*iso*butylene system, $[SnCl_4]$ 0·02 moles/l. Total monomer concentration 2·5 moles/l.

styrene system, in the direction of a higher initial content of active monomer. Thus, the highest velocities in the styrene-*iso*butylene system are obtained at a molecular ratio of styrene to *iso*butylene of 2·5 : 1, while in the styrene-α-methylstyrene system they lie in a region of much lower initial content of α-methylstyrene.

The kinetic curves of the polymerization for molecular ratios of styrene to *iso*butylene of from 2·5 : 1 to 50 : 1 are shown in Fig. 12.

In Fig. 13 is shown the dependence of the induction period observed on the concentration of isobutylene.

Polymerization of styrene at 40°. Styrene is one of the most widely studied monomers. A series of investigations has been devoted to the separate polymerization of styrene by a cationic mechanism with various catalysts, solvents and additives [1, 3–8]. However, the majority of the previous investigations were carried out at temperatures not exceeding 30° and at monomer concentrations not higher than 1·8 moles/l., comparatively low conversions being obtained.

In the work of two of us [1], the polymerization of styrene at 20° and a concentration of monomer of 2·5 moles/l. with $SnCl_4$ catalyst in ethyl chloride proceeded with some increase of velocity with time; however, at a catalyst concentration of 0·002 moles/l. it was not very well-marked and began some hours after the beginning of the reaction.

We carried out the polymerization of styrene at 40° (monomer concentration, 2·5 moles/l.; $SnCl_4$ concentration, 0'002 moles/l.). The kinetic curves obtained under these conditions have an appearance similar to the polymerization curves

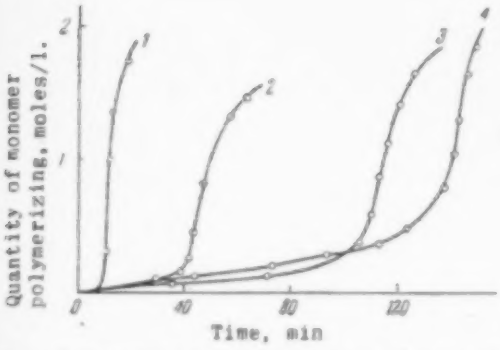

FIG. 12. Velocity of copolymerization of the styrene-*iso*butylene system for small concentrations of *iso*butylene at 0°. $[SnCl_4]=0{\cdot}002$ moles/l. Initial molar ratio of styrene to *iso*butylene: (1) 2·5:1; (2) 10:1 (3) 20:1; (4) 50:1.

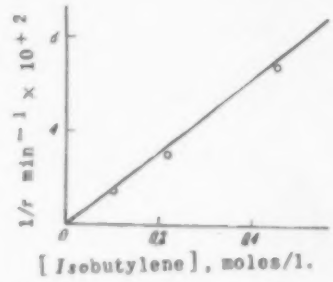

FIG. 13. Dependence of the induction period on the concentration of *iso*butylene. $[SnCl_4]=0{\cdot}002$ moles/l. Total monomer concentration, 2·5 moles/l.

of styrene at lower temperatures in the presence of small quantities of a more active monomer—α-methylstyrene or *iso*butylene (Fig. 14).

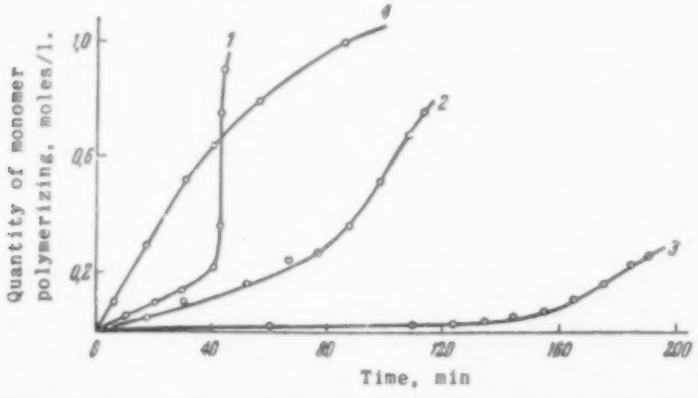

FIG. 14. Separate polymerization of styrene and α-methylstyrene at 40°·$[SnCl_4]$ 0·002 moles/l.: (1) 2·5 moles/l. styrene; (2) 1·5 moles/l. styrene; (3) 1 mole/l. styrene; (4) 2·5 moles/l. α-methylstyrene.

The effect of the increase in the velocity of polymerization of styrene with time, in addition to its pronounced temperature dependence, is characterized also by a considerable dependence on the initial concentration of monomer

(Fig. 14), while the induction period proves to be inversely proportional to the styrene concentration (Fig. 15).

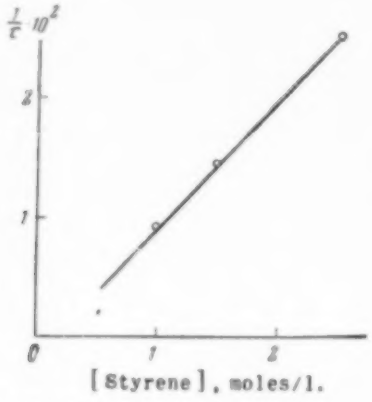

FIG. 15. Dependence of the induction period on the concentration of styrene; $[SnCl_4] = 0{\cdot}002$ moles/l., 0°.

By measuring the molecular weights of the polystyrene obtained at 40°, it was established that the observed increase in the velocity of polymerization is not accompanied by an increase in the length of the molecular chain and, consequently, is produced by an increase in the velocity of initiation. As in the case of the styrene-α-methylstyrene system, the addition of H_2O destroys the acceleration effect. (Fig. 16).

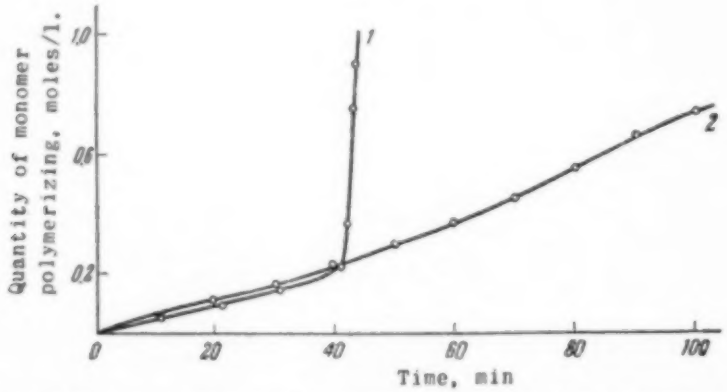

FIG. 16. Influence of water on the acceleration effect in the polymerization of styrene. $[SnCl_4] = 0{\cdot}002$ moles/l., styrene = 2·5 moles/l., 40°: (1) in the absence of water; (2) in the presence of 0·006 moles/l. water.

Styrene-n-butyl vinyl ether system. Study of the styrene-α-methylstyrene and styrene-*iso*butylene systems has shown that small additions of the more active

monomer to the styrene cause a sharp increase in the velocity of polymerization of the latter. In connection with this, interest was presented by an investigation of the kinetics of copolymerization of styrene with one of the most active monomers for cationic polymerization, *n*-butyl vinyl ether. It has been shown by us that the separate polymerization of *n*-butyl vinyl ether and its copolymerization with styrene with $SnCl_4$ as catalyst proceeds with very great velocity. On the introduction of the catalyst, the reaction mixture becomes warm and acquires a dark red and then a violet colour. Even in the polymerization of a mixture containing 50 moles of styrene to 1 mole of the ether, the initial velocity is so great that the bulk of the ether polymerizes in the first few minutes.

The styrene-*n*-butyl vinyl ether system has two characteristic features: (1) the polymerization ceases after all the ether has been used up; (2) the colour of the solution changes as the reaction proceeds from yellow through orange and red to violet.

CONCLUSIONS

(1) The cationic copolymerization of the three systems styrene-α-methylstyrene, styrene-*iso*butylene, and styrene-*n*-butyl vinyl ether, and also the separate polymerization of styrene at 40°, have been investigated.

(2) The copolymerization constants obtained for the systems styrene-α-methylstyrene and styrene-*iso*butylene have been calculated.

$$\alpha = 0{\cdot}05 \text{ (styrene)}, \quad \beta = 2{\cdot}90 \text{ (α-methylstyrene}$$

$$\alpha = 0{\cdot}17 \text{ (styrene)}, \quad \beta = 1{\cdot}60 \text{ (}iso\text{butylene)}.$$

(3) In the study of the velocities of copolymerization, a partial reduction of the initial velocities of polamerization in the region of a small content of the more active component, connected with a decreased velocity of chain building, has been discovered.

(4) A sharp increase with time in the velocity of polymerization of styrene in the presence of small amounts of the more active monomer *iso*butylene or α-methylstyrene, and also in the case of the separate polymerization of styrene at 40°, has been discovered. On the basis of the measurement of molecular weights it has been shown that the acceleration effect is connected with an increase in the velocity of initiation.

(5) The influence of the temperature, the concentrations of the components, additions of H_2O and HCl and the nature of the solvent on the acceleration effect have been investigated.

Translated by B. J. Hazzard

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CHARACTERISTICS OF THE MECHANISM OF CATIONIC POLYMERIZATION— II. ON THE MECHANISM OF THE ELEMENTARY REACTIONS OF CATIONIC POLYMERIZATION*

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(*Received* 1 *June* 1959)

IN the preceding communication [1] the results of an experimental study of the cationic copolymerization of styrene with other monomers were reported. In the present communication is given a discussion of the results obtained.

Relative reactivity of the monomers. As follows from the results obtained earlier (see [1], Tables 1 and 2), the copolymers of styrene with α-methylstyrene and of styrene with *iso*butylene are greatly enriched in the more active component-α-methylstyrene or isobutylene. The enrichment is considerably greater in the region of a small initial content of the more active monomer. This is explained by the steric hindrances arising in the interaction of the monomer possessing two substituents on a carbon atom of the double bond with its own carbonium ion. A steric effect manifests itself also in the separate polymerization of these monomers in the form of a reduced heat effect of the reaction, [2, 3]. The values of the copolymerization constants for the systems studied also bear witness to presence of steric hindrances. According to the copolymerization constant, the reactivity of the molecules of α-methylstyrene and *iso*butylene relative to the carbonium ion of styrene is considerably higher than that relative to their own carbonium ions.

On the basis of the values of their copolymerization constants, the monomers studied may be placed in the following series according to their reactivity: α-methylstyrene > *iso*butylene > styrene.

Inhibiting effect. In the styrene-α-methylstyrene system [1], for example, it was shown that small additions of the more active monomer to styrene caused a reduction in the initial velocity of polymerization of the styrene (see [1], Fig. 3), accompanied by a reduction in the molecular weight. The effect of partial inhibition of the polymerization of the less active monomer by small additions of the more active monomer is well known in radical polymerization. It is explained by the inverse relationship between the activities of the monomer and the radical corresponding to it.

* Vysokomol. soedin. 1: No. 9, 1343–1350, 1959.

In ionic polymerization, in consequence of the absence of a method of determining the individual constants of chain-formation and chain-breaking, such inverse relationships cannot be established by direct methods. The effect observed by us of the reduction in the initial velocity of polymerization of styrene by small additions of α-methylstyrene is an indirect indication that such inverse relationships also takes place here.

The effect of the increase in the velocity of polymerization with time. The increase in the velocity of polymerization with time observed by us in the styrene-α-methylstyrene and styrene-*iso*butylene systems, and also in the separate polymerization of styrene at higher temperatures [1], has an apparent analogy in radical polymerization; however, this analogy is only superficial. The velocity increase in radical polymerization is observed on the attainment of considerable degrees of conversion and is connected with the difficulty of recombination of the radicals on an overall increase in the viscosity of the system. It is accompanied by an increase in the molecular weight.

The acceleration effect investigated by us, as has been shown, is connected with a sharp increase in the velocity of initiation of the polymerization and is therefore specific for cationic polymerization*.

The similarity of the kinetic for curves for the case of the polymerization of styrene in the presence of small additions of a more active monomer and that of its seperate polymerization at higher temperatures leads to the conclusion that a general cause lies at the bottom of the observed velocity increase effects. Small additions of active monomers only spread the field in which the acceleration effect is displayed in the direction of lower temperatures. The fact that such small additions of α-methylstyrene and *iso*butylene as 1:20 and 1:50 with respect to the styrene causes a ten-fold increase in the velocity of polymerization of the latter leads to the conclusion that selective complex formation of the catalyst with the more active monomer is here taking place.

The majority of catalysts for cationic polymerization—halides of Al, B, Ti, Sn, Sb and Fe—being co-ordinately unsaturated, are capable of forming a series of complex compounds with various molecules (H_2O, HCl, benzene, ethers, alcohols and amines). π-Complexes of catalysts of this type with olefins are also known [4,-8]. Recently the formation of a π-complex of $SnCl_4$ with *cyclo*hexene was established by Terinin and co-workers [9, 10] (frequency of the double bond of *cyclo*hexene lowered by 115–125 cm^{-1} through the interaction of its π-electrons with the $SnCl_4$). Taking into account the electron-accepting nature of the catalyst and the electron-donating nature of the monomer in cationic polymerization, two of us in 1949 [11] arrived at the conclusion that the catalyst is present in the

* This increase in the velocity of polymerization is many times greater than a certain increase in the velocity of polymerization caused by a rise in the mean degree of polymerization on the exhaustion of the small additions of α-methylstyrene in the course of the reaction.

solution of the monomer in the form of a π-complex with it, and initiation is accomplished through the interaction of this π-complex with a molecule of monomer [12].

We conjecture that, in a solution containing a relatively high molar proportion of styrene, on mixing the monomers with the catalyst complexes of the $SnCl_4$ with the styrene are formed. Since the co-ordination number of Sn^{IV} is 6, the $SnCl_4$ molecule can add on two molecules of styrene.* However, the addition of the second molecule of styrene to the π-complex requires, apparently, a considerable activation energy in consequence of which this process proceeds with an appreciable velocity only at a higher temperature.

The more active monomers—π-methylstyrene and isobutylene—, having a greater density of the electron cloud on the double bond, are more prone to complex formation than styrene and, apparently, can add on to the $SnCl_4$-styrene complex at lower temperatures.†

Schemes of the initiation processes for the cases considered may be represented in the following way.

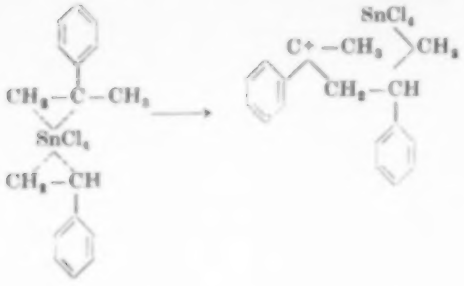
I. The polymerization of styrene in the presence of small additions of α-methylstyrene.

1. $SnCl_4 + CH_2=CH$(C$_6$H$_5$) $\longrightarrow$ $SnCl_4$ CH_2-CH(C$_6$H$_5$) (Fast stage)

2. $SnCl_4$ CH_2-CH(C$_6$H$_5$) $+ CH_2=$ C(CH_3)(C$_6$H$_5$) $\longrightarrow$ CH_2-C(CH_3)$_2$-C$_6$H$_5$ $SnCl_4$ CH_2-CH(C$_6$H$_5$)

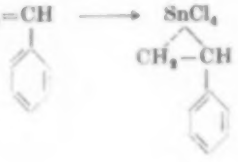
* As is well-known, $SnCl_4$ forms complexes with various molecules containing electron-donating groups. In these complexes the co-ordination number of the Sn is 6. Examples of such compounds are the complexes of $SnCl_4$ with pyridine ($SnCl_4 . 2Py$) and with ethers and esters ($SnCl_4 . 2$ eth. or $SnCl_4 . 2$ est.), which possess a *cis*-structure.

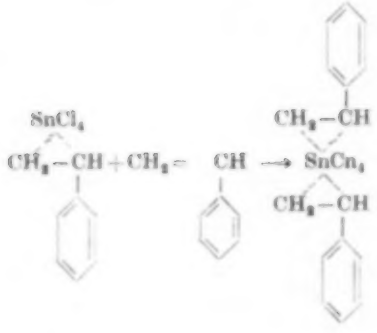
† It is possible that the π-complex of catalyst and styrene is also bound with one molecule of the solvent. In this case the addition of a second molecule of styrene will involve the displacement of the solvent molecule by the monomer. However, according to the kinetic results, if such complexes of catalyst with ethyl chloride exist they are relatively unstable and do not influence the kinetic process.

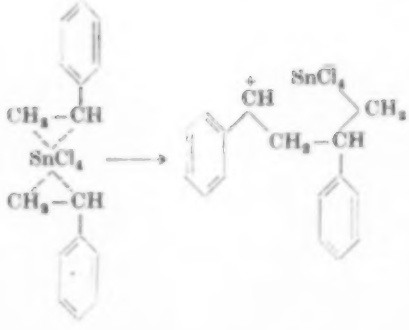
3. 

(Initiation)

II. The polymerization of styrene at 40°

1. $SnCl_4 + CH_2=CH$  (Fast stage)

2. 

3. 

(Initiation)

Chain-building and chain-breaking proceed in the usual way. It has been found (see [1], Fig. 5, 6, 13, and 15) that the length of the stationary period τ depends on the concentrations of the components in the following way.

(1) For the polymerization of styrene in the presence of small additions of α-methylstyrene.

$$\frac{1}{\tau_1} = k_1 [SnCl_4] \cdot [\alpha\text{-methylstyrene}]$$

and it does not depend on the concentration of the styrene.

(2) For the polymerization of styrene in the presence of small additions of *iso*butylene

$$\frac{1}{\tau_1} = k_2 [SnCl_4] \cdot [iso\text{butylene}]$$

and it does not depend on the concentration of the styrene.

(3) For the separate polymerization of styrene at 40°

$$\frac{1}{\tau_1} = k_3 [SnCl_4] \cdot [\text{styrene}].$$

If it is assumed that $[SnCl_4]=[SnCl_4 \cdot \text{styrene}]$ (which follows from the kinetic results), then the dependence of τ on the concentrations of the components which is obtained indicates that the time τ is connected with the velocity of formation of the binary complexes of the catalyst with the monomers. In the presence of the binary complexes the initiation process a unimolecular reaction and proceeds with higher initiation velocities in comparison with the bimolecular initiation mechanism in the presence of simple complexes.

In order to confirm the proposed mechanism, we conducted an experiment in which the order of the formation of the complex was varied. The catalyst was introduced into the solvent with a small quantity of α-methylstyrene, the solution was allowed to stand for a time equal to the induction period under these conditions* and then a large quantity of styrene was added. Here there was a failure to attain such high velocities as when the monomers are mixed simultaneously. As should be expected, the initial velocity here was considerably higher than the initial velocity observed with the usual order of mixing of the monomers and the increase in velocity with time was not very great (Fig. 1).

With the usual order of mixing of the monomers, it is assumed that the initiation is accomplished by means of the $SnCl_4$-styrene complex, while with the initial introduction of α-methylstyrene the $SnCl_4$-α-methylstyrene complex is formed, which is more active in the initiation. Transformation of the $SnCl_4$-α-methylstyrene complex into a binary complex through the addition of a further molecule of α-methylstyrene is not very probable on account of the fact that, as follows from the above-mentioned results, α-methylstyrene does not form a binary complex even at 40°. The addition of a molecule of styrene as a second

* It was shown in a control experiment that the polymerization of α-methylstyrene under these conditions is negligible.

molecule proceeds with measurable speed only at higher temperatures. A certain increase in velocity taking place in this experiment is, apparently, partially explained by an increase in the velocity of chain-building as the α-methylstyrene becoms exhausted.

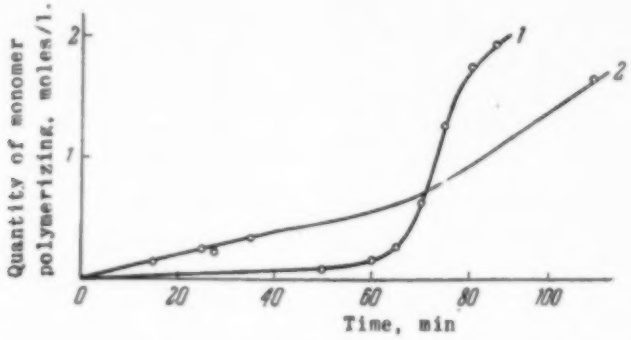


FIG. 1. Experiments on variation in the order of addition of the monomers. $[SnCl_4] = 0{\cdot}002$ moles/l. Total concentration of monomers, 2·5 moles/l. Initial molar ratio of styrene to α-methylstyrene, 20:1, 0°; (1) monomers added simultaneously; (2) α-methylstyrene added previously.

The explanation of the increase in the velocity of polymerization in the systems investigated by the formation of binary complexes of the catalyst with the monomers finds confirmation in the inhibiting action of additions of H_2O and HCl on this effect (see [1], Fig. 4). The formation of π-complexes of the monomers with the catalyst under these conditions is hindered by the competing formation of complexes with molecules of H_2O and HCl, which are capable of giving very stable complexes with the catalyst. Various authors, during investigations of the cationic polymerization of styrene with $SnCl_4$ in different non-polar solvents [13–16] have observed induction periods in the course of which no polymerization takes place. Okamura and co-workers report that the direct proportionality between the length of the induction period and the concentrations of catalyst and monomer observed by them are explained by a reduced velocity of formation of monomer –catalyst complexes in weakly polar solvents.

The presence of induction periods with waekly polar solvents makes it possible to compare the complex-forming capacities of styrene and α-methylstyrene. It can be seen from Fig. 10 [1], that even at low concentrations of catalyst the induction period is almost absent in the case of α-methylstyrene, while in the case of styrene it amounts to 1·5 hr. These results confirm our hypothesis concerning the great capacity for complex-formation of α-methylstyrene in comparison with styrene. In consequence of the sharp reduction in the velocity of formation even of simple complexes in weakly polar solvents, the formation of binary com-

plexes under these conditions is not very likely. This is confirmed by the experimental results. As can be seen from Fig. 9 [1], at 0° no acceleration of the process in tne polymerization of styrene in the presence of small quantities of α-methylstyrene can be observed.

From the results of the copolymerization constants for *iso*butylene and α-methylstyrene with styrene it follows that the reactivity of a molecule of *iso*butylene relative to the styrene carbonium is less than the reactivity of α-methylstyrene.

Assuming that in cationic polymerization there is direct relationship between the capacity of the monomer for complex-formation and its reactivity, it can be concluded that the capacity of isobutylene for complex-formation with $SnCl_4$ is less than for α-methylstyrene. From the point of view of the different capacities for complex formation of α-methylstyrene and *iso*butylene, the different dependence of the increase in velocity of polymerization effect on the initial ratio of the monomers in the case of the styrene-α-methylstyrene and styrene-*iso*butylene systems becomes clear.

The greatest maximum velocities of polymerization in the styrene-*iso*butylene system were observed at a styrene to *iso*butylene ratio of 2·5:1, while in the styrene-α-methylstyrene system the greatest values of the velocities were obtained with a considerably lower content of α-methylstyrene. *Iso*butylene, as the less active monomer, forms, apparently, less stable complexes with $SnCl_4$ than α-methylstyrene. In the styrene -α-methylstyrene system at ratios of styrene to α-methylstyrene of 2·5:1 and 4:1 all the $SnCl_4$ is bound in the complex with the α-methylstyrene and no formation of a binary complex and, consequently, no acceleration of the process is observed with these ratios.

It can be assumed that in the styrene-*iso*butylene system, in view of the lower stability of the $SnCl_4$-*iso*butylene complexes, a definite equilibrium distribution of the $SnCl_4$ between its complexes with the *iso*butylene and with the styrene exists. The presence of the complexes with styrene creates the conditions for the formation of binary complexes, which leads to the effect of a sharp increase in velocity at these ratios. Comparison of the results for the styrene-*iso*butylene system with the results for the styrene-*iso*prene system obtained earlier [17] indicates the considerable similarity in the curves of the dependence of the maximum velocity of polymerization on the initial monomer ratio. The greatest value of the maximum velocities in the styrene-*iso*prene system lies in the same region of concentrations and their absolute value is of the same order as for the styrene-*iso*butylene system. The similarity in behaviour of *iso*prene and *iso*butylene is explained by the similarity of the structure of the complexes formed with *iso*butylene and with *iso*prene where the addition takes place in the 1,2 position. It must, however, be noted that *iso*butylene, as a more active monomer than *iso*prene, is a better complex-former, in consequence of which the formation of the styrene-$SnCl_4$-*iso*butylene binary complexes takes place at a relatively low molar proportion of *iso*butylene (at ratios of styrene to *iso*butylene of 20:1 –50:1).

The proposed initiation mechanism makes it possible to explain a series of kinetic effects which were observed in previous work on the separate polymerization of *iso*prene [18] and its copolymerization with butadiene [19]. Thus, it was discovered that the separate polymerization of *iso*prene at 0° proceeds with an increase of velocity with time. This effect increases sharply with a rise in the concentrations of catalyst and monomer.

The molecule of *iso*prene has two double bonds—in the 1,2 and 3,4 positions—which differ in π-electron density in consequence of the presence of a CH_3 group on the second carbon atom, and therefore a solution of *iso*prene* may be considered as a solution of two monomers of different activities taken in a molar ratio of 1:1. It may be assumed that, in consequence of the higher electron density, the 1,2 bond is more active in cationic polymerization and correspondingly in the formation of π-complexes with $SnCl_4$. Hence, in a solution of $SnCl_4$ in *iso*prene, the relative concentration of the 3,4 complexes is, apparently, low. These complexes formed by $SnCl_4$ with the 3,4 bond of *iso*prene can be converted into binary complexes by means of the addition of a second molecule of *iso*prene at the 1,2 position, which leads to an increase in the velocity of polymerization with time. The greater the concentrations of catalyst and monomer, the greater the absolute concentration of the 3,4 complexes and the greater the acceleration effect. The transformation of the complexes of $SnCl_4$ with the 1,2 double bond of the *iso*prene into binary complexes by reaction with a second molecule of *iso*prene is (by analogy with *iso*butylene and α-methylstyrene) hindered on steric grounds. On the addition of butadiene to a solution of *iso*prene we increase the number of simple complexes which can be transformed into binary complexes by the addition of a molecule of *iso*prene and by that very fact must increase the acceleration effect, which was observed in an experiment.

Analysis of the results given indicates that, for the catalyst $SnCl_4$, there exists some dependence of the capacity of the monomers for complex-formation, which was observed earlier by Anderson [6], Gel'man [20] and Winstein and Lucas [8] for compounds of Pt and Ag, which is explained, apparently, by the different nature of the bond of the complex formed. Thus, for example, Anderson gives for the capacities of monomers for complex-formation in the case of complexes of platinum chlorides with unsaturated compounds: ethylene>styrene>α-methylstyrene. Winstein and Lucas for silver salts and Gel'man for platinum salts obtained a similar dependence of the capacity of a monomer for complex-formation on its structure.

From these results it follows that, for salts of platinum and silver, the capacity of monomers for complex-formation decreases with an increase in the number of electropositive substituents on a carbon atom linked by the double bond, which is in conformity with the hypothesis on the structure of these complexes put forward by Dewar and developed by Chatt.

* "isobutylene" in the original (Translator)

The reverse order of monomers in respect of their capacity for complex-formation with $SnCl_4$ which we obtained α-methylstyrene>*iso*butylene>*iso*prene>butadiene, styrene) bears witness to the fact that these molecular compounds are π-complexes in which predominates a type of bond explained only by a displacement of the π-electrons towards the Sn atom. The interaction of the *d*-electrons of these elements with unsaturated molecules proposed for Pt and Ag is thus, apparently, absent.

It was shown earlier [1] that the styrene-vinyl *n*-butyl ether system differently from the styrene-α-methylstyrene and styrene-*iso*butylene systems.

The peculiarities of the polymerization of the styrene-vinyl *n*-butyl ether system become clear if two factors are taken into account: (1) the very high activity of the double bond of the ether; (2) the ability of the ether to form extremely stable complexes by means of the ethereal oxygen atom [22].

The high activity of the double bond of vinyl *n*-butyl ether leads to a very high reaction velocity, thanks to which the whole mass of it is polymerized in the first few minutes after the beginning of the reaction. On the other hand, this activity of the double bond must give fairly stable complexes with the catalyst (more stable than the complexes through the oxygen atom) which also affect the polymerization. After the ether is exhausted, the whole of the $SnCl_4$ proves to be linked to the oxygen atoms of the copolymer formed. The polymerization of styrene does not take place in the presence of such complexes.

The change of colour of the solution observed in the course of the reaction

is connected, apparently, with the fact that the complexes and also the carbonium ions of the vinyl *n*-butyl ether possess different colours.

As follows from the kinetic results which we obtained, the high initiation velocities observed by us in the above-mentioned systems are connected with the essential role of the binary complexes of $SnCl_4$ with the monomers in the initiation processes. It follows from the results of the separate polymerization of α-methylstyrene and isobutylene that the formation of such binary complexes from monomers containing two substituents on one of the carbon atoms linked by the double bond (*iso*butylene, α-methylstyrene) is hindered on steric grounds.

The presence of a simple complex consisting of a molecule of catalyst and of a monomer containing only one substituent on a carbon atom linked by the double bond and, as a rule, relatively unreactive in the polymerization is essential for the production of such binary complexes. Then the formation of the binary complex may take place either by means of the addition of a second molecule of the same monomer at elevated temperatures or by the addition of

small admixtures of monomers which are more active in complex-formation and polymerization (α-methylstyrene, *iso*butylene), which leads to the formation of a binary complex with molecules of different monomers.

CONCLUSIONS

The question of the mechanism of carbonium polymerization in the instance of the two systems styrene-α-methylstyrene and styrene-*iso*butylene has been investigated.

The copolymerization constants of these pairs of monomers, characterizing the relative reactivity of the monomers, were obtained. It was shown that in cationic polymerization, as in radical polymerization, the activity of the carbonium ion inverse relationship to the activity of the monomer.

The specific characteristics of the polymerization of styrene in the presence of small additions of α-methylstyrene and *iso*butylene were established.

The effects consisting of a sharp increase in the initiation velocity for styrene in the presence of small additions of a more active monomer even at relatively low temperatures and in the velocity of the separate polymerization of styrene at elevated temperatures were discovered. The selective complex-formation of the monomers with the catalyst was shown by direct experiments.

On the basis of an analysis of the experimental results, the effects consisting of a sharp increase in the initiation velocity of styrene in the presence of small additions of a more active monomer and also in the velocity of the separate polymerization of styrene at elevated emperatures have been explained with the use of a hypothesis on the formation of complexes of the catalyst with two molecules of monomer.

The results given are in agreement with ideals developed earlier on the possible course of cationic polymerization without the addition of a co-catalyst and point the way to the realization of high velocities of cationic polymerization.

Translated by B. J. HAZZARD

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VOL.
1
1960

MACRORADICAL STUDIES IN POLYMERIZATION AND DEGRADATION PROCESSES II*

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(*Received* 22 *June* 1959)

MACRORADICALS IN THE POLYMERIZATION PROCESS

SOME results of the use of the electron paramagnetic resonance spectroscope in a macroradical investigation of the photopolymerization of methyl methacrylate (MMA) were reported in a previous communication [1]. Now vinyl acetate (VA), methyl acrylate (MA), methacrylic acid (MMA) and acrylic acid (AA) have been studied by a similar method. The procedure and the experimental apparatus have been described in [1].

Unsensitized photopolymerization was carried out at 7°C in quartz bulbs with a diameter of 2·5 mm. A PRK-4 mercury lamp was used as the source of illumination. In order to study the spectrum, the initiation process was interrupted from time to time and the bulbs were transferred to the absorption cell of the radiospectrometer. The extent of conversion was determined from the consumption of electric power in the system [1].

In the polymerization of VA and MA, as in the case of MMA, macroradicals appeared in appreciable quantity ($<10^{-6}$ moles/l.) at a degree of conversion of 50–60 per cent; then their concentration rose rapidly and at the moment of completion of the process attained $=2\times10^{-3}$ moles/l. for VA and $\approx0{\cdot}5\times10^{-3}$ moles/l. for MA. Typical kinetic curves are shown in Fig. 1 and the appearance of the spectra in Fig. 2.

If the initiation is discontinued, the polymerization also ceases practically immediately even though there may be a considerable quantity of monomer left and a high concentration of macroradicals in the system. The spectra observed in this way and under these conditions relate to "trapped" radicals capable only of extremely slow addition of the monomer and recombination.

It is impossible to explain the accumulation of trapped radicals in such homogeneous systems as polymerizing MMA, VA and MA at comparatively early stages of the process from the point of view of the usual ideas on the kinetic growth and destruction of the macroradicals. Apparently the reaction centres of a considerable number of high-molecular radicals become difficult to approach

* Vysokomol. soedin. 1: No. 9, 1374–1382, 1959.

because of the convolution of the mass of macroradicals. If the system is again subjected to irradiation, polymerization proceeds with the previous velocity; this indicates that the newly formed "live" comparatively low-molecular radicals are capable of a rapid addition of the monomer.

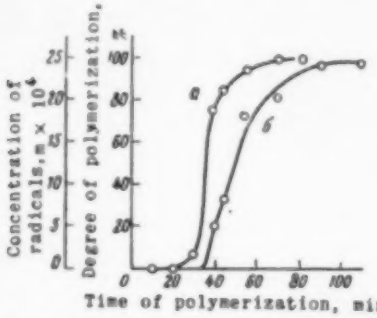


FIG. 1. Kinetics of the photopolymerization of vinyl acetate at 7°: (a) degree of conversion; (b) concentration of macroradicals.

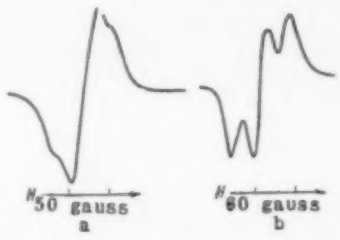


FIG. 2. EPR spectra of macroradicals: (a) vinyl acetate, (b) methyl acrylate.

It must be of fundamental importance for trapping the radicals, how good or bad a solvent the monomer or the corresponding polymer is. Hence the phenomenon of trapping appears at different stages with different monomers.

In contrast to MMA, the greater part of the radicals of which prove to be stable at room temperature, the concentration of the macroradicals of VA and particularly MA diminishes with appreciable velocity (Fig. 3). The kinetics of this process for MA obey a hyperbolic law, resulting from a bimolecular mechanism of recombination or disproportionation of the radicals.

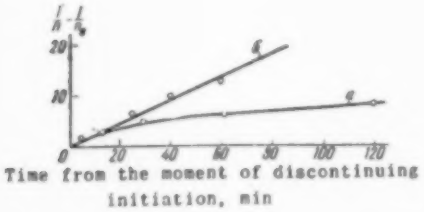


FIG. 3. Kinetics of the destruction of trapped radicals at room temperature: (a) vinyl acetate, degree of conversion 80 per cent; (b) methyl acrylate, degree of conversion 100 per cent (n is the concentration of radicals in arbitrary units).

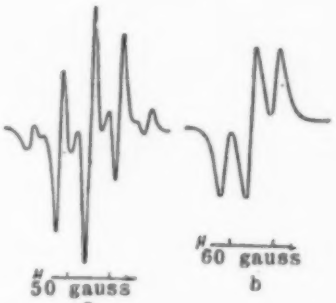


FIG. 4. EPR spectra of macroradicals: (a) methacrylic acid; (b) acrylic acid.

In the photopolymerization of MMA and AA, where the polymer formed separates out as a precipitate, part of the macroradicals are trapped in the

gel and EPR spectra are observed even in the early stages of the process. The spectrum of MMA (Fig. 4, a) does not differ at all from the spectrum of MMA [1, 2], and that of AA (Fig. 4, b) from that of MA. This confirms Ingram's hypothesis [3] that the protons of the ester group do not interact with the unpaired electron.

The radicals trapped in the polymerized acids are much more stable than in the polymers of the corresponding esters; for example, the EPR spectrum in poly-(methacrylic acid) remains unchanged for tens of minutes even at 180°. This stability is explained by the difficulty of diffusion in these polymers, the links of which form hydrogen bonds with their neighbours.

MACRORADICALS IN THE MECHANISM OF THE DEGRADATION OF POLYMERS

Earlier [4] we published the first results of an investigation of the macroradicals arising in the newly-formed surfaces during the mechanical disintegration of polymers below the glass temperature. This work has now been extended.

The disintegration was carried out by milling the samples with a conical cutter under the surface of liquid nitrogen. The shavings obtained were transferred without defrosting to the absorption cell of the spectrometer.

EPR was observed in all cases; the quantity of radicals was comparable with the number of macromolecules exposed in the newly-formed surfaces.

Polyethylene, polystyrene and thiokol. Low-pressure polyethylene after degradation in liquid ammonia gives a spectrum with a clearly resolved hyperfine structure, revealing saturation at the power of a high-frequency generator of the order of 50 mW (Fig. 5, a and b). This spectrum undouptedly appertains to a hydrocarbon radical; a possible structure of this radical is given in [4].

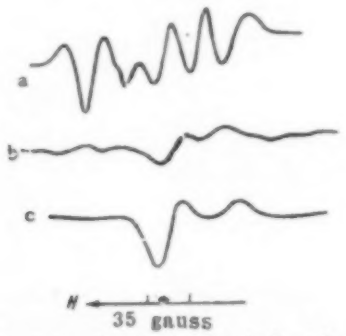


FIG. 5. Spectrum of the macroradicals of polyethylene formed in mechanical disintegration: (a) low-pressure polyethylene, generator power 0·5 mW; (b) ditto, generator power 50 mW; (c) high-pressure polyethylene, generator power 0·5 mW.

A completely different picture is observed under the same conditions with high-pressure polyethylene (Fig. 5, c). A similar unsymmetrical absorption band

not revealing saturation is characteristic for radicals with a reaction centre on an oxygen atom (ROO· or RO· type).

A similar difference in spectra was observed with the mechanical degradation of ordinary polystyrene from a radical polymerization and polystyrene obtained in the absence of oxygen (with an organometallic catalyst) (Fig. 6); then only the spectrum of the radical ROO· or RO· was observed in the first case and a triplet with the spacing between the neighbouring lines ≈34 gauss in the second case.

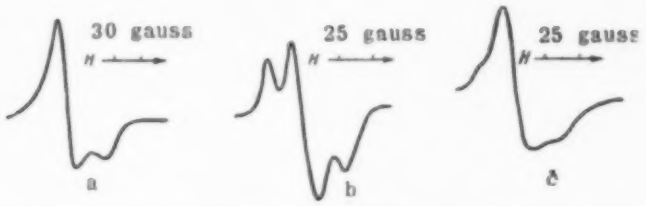


FIG. 6. Spectrum of the macroradicals of polystyrene formed in mechanical disintegration (a) conventional polystyrene, generator power 0·5 mW; (b) polystyrene obtained with a Ziegler catalyst, generator power 0·5 mW; (c) ditto, generator power, 50 mW.

The differences between the polymers in the two cases may consist in the fact that in the samples of polystyrene and polyethylene obtained in non-oxygenated conditions inclusions of oxygen in the main chain of the molecule are lacking. For high-pressure polyethylene, which is polymerized with oxygen as the initiator [5], the presence of such inclusions is possible. In the radical polymerization of styrene in the presence of oxygen, the inclusion of O_2 linkages in the covalent chain has been observed [6]. Since mechanical disintegration is carried out with the use of relatively little energy, the breaks in the polymer chains must take place at the weakest links, which are constituted by the oxygen

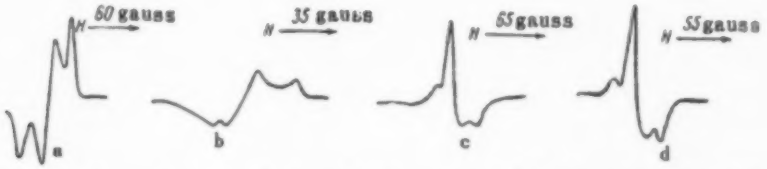
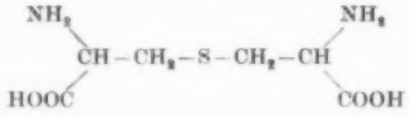


FIG. 7. Spectrum of macroradicals arising in mechanical disintegration: (a) thiokol, (b) polycaprolactam, (c) polyvinyl acetate, (d) polymethyl acrylate.

inclusions in the main chain. It is well known that the energy of the O—O bond (≈34 kcal/mole) is much less than the energy of the C—C bond (≈76 kcal/mole). The result of the breakages at an O—O or C—C bond is the appearance of the structureless spectrum of radicals with an unpaired electron centring on the electronegative oxygen atom.

The hypothesis of predominating breakages of the chain at the weak linkages received further support from a study of the degradation of thiokol, which has the structure ~~~~$CH_2-S-S-CH_2-S-S$. With this, an unsaturated tripled was observed (Fig. 7, a) with a distance between the extreme lines ≈ 90 gauss and characteristic for a mean g-factor appreciably greater than 2 (2·015); probably it appertains to the radical ~~~CH_2-S· with a reaction centre on the sulphur atom, formed in the breakages of the molecules of the polymer at the weak S—S linkages. A similar spectrum was observed, but not explained, by Shields and Gordy [7] in irradiated lenthionine, which has the structure



Polycaprolactam. In the mechanical disintegration of polycaprolactam there is produced a considerably smaller (by about two orders of magnitude) quantity of radicals than with the majority of other polymers ($\approx 10^{15}$ spins/g). However, in this case also, on increasing the sensitivity of the spectrometer the hyperfine structure of the EPR spectrum could always be detected (Fig. 7, b), connected, possibly, with the nucleus of the nitrogen N^{14} (the triplet spectrum is observed in the region of the unsymmetrical line of the oxygen radical).

Other polymers. Hyperfine structure was observed in the spectra of many of the radicals studied. Traces of a triplet spectrum similar to those obtained during polymerization are observed in the EPR spectra on mechanical disintegration of polyvinyl acetate and polymethyl acrylate (Fig. 7, c and d).

In view of the relatively complex picture and the interfering influence of the oxygen radicals, further work on the analysis of the structure of many of the spectra observed is necessary. Apparently, in a series of cases, the radicals formed in the breaking of the macromolecules are active enough to react with the oxygen contained in the system (the liquid nitrogen used for cooling contained up to 10 per cent of O_2) and, possibly, with the surrounding molecules. Some radicals which are undoubtedly formed in the breaking of chains, for example, with an unpaired electron on a methylene group R—CH_2, can never be observed.

It is possible to prevent secondary reactions of the active radicals by lowering the temperature further.

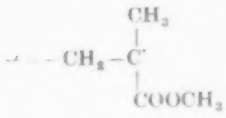
It can be seen from the examples considered that the method of mechanical disintegration makes it possible to determine the weak points in polymer chains if the EPR spectra obtained permit the identification of the radicals formed. On the other hand, if the weak points in the chain are known, it is possible to forecast the type of radicals formed. The spectra obtained on mechanical disintegration can serve as a standard for other investigation. The proposed method has great advantages in this respect over the method used hitherto

of creating macroradicals in a solid phase by means of irradiation with penetrating radiation since in the latter case it is rarely possible to forecast accurately just what radicals will be formed.

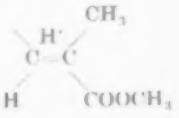
THE STRUCTURE OF MACRORADICAL SPECTRA

The nature of the radicals trapped in a polymer gel and created by mechanical disintegration is usually known with satisfactory accuracy. This makes it possible to use the results of EPR spectroscopy for elucidating the structure of the macroradicals.

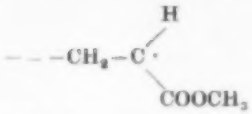
The spectra of MMA observed by us during homogeneous polymerization in the absence of a solvent [1] and on mechanical disintegration [4] are identical in their main features with one another and also with the spectra published earlier obtained in the γ-irradiation of the polymer and in the polymerization of the monomer, [2, 3]. The spectrum consists of five main lines corresponding of the interaction of an unpaired electron with four equivalent protons (ratio of the intensities in the multiplet 1 : 4 : 6 : 4 : 1). The question arises, how, with the radical structure



the electron interacts with four and not with five protons. It is possible to give the following quantum-chemical explanation to this. The unpaired electron can interact with the protons bound not to the carbon atoms shown but to the neighbouring ones as a result of the phenomenon of hyperconjugation. This means that the wave function of the radical, calculated by the method of localized pairs, will contain those components in which the C—H bonds have donated an electron to a C atom for the formation of a π-electron pair connecting two adjacent carbon atoms, that is, structures of the type



Since in the formation of the virtual double bond all the valencies of both the C atoms are coplanar, the two H atoms of the methylene group cannot simultaneously participate in similar structures. As far as concerns the three protons of the methyl group, they may, with equal probability, participate in the formation of similar structures since the methyl group rotates with a frequency much greater than the frequency of the Zeeman transition for an unpaired electron. This explanation is confirmed by the fact that with MA and AA similar triplet spectra are observed which correspond to the interaction of the electron spin with the two equivalent protons in a radical of the type



(Fig. 2, b and 4, b). This triplet is present, roughly speaking, in the classical ratio of intensities 1 : 2 : 1 with a spacing between neighbouring lines of 29 gauss (the corresponding figure for PMMA and PMMA is 27 gauss). Similar triplets are also observed with the macroradicals of polystyrene and poly-(vinyl acetate). The comparatively small magnitude of the separation in the latter case can be explained by a displacement of the electron cloud in the direction of the electronegative oxygen atom.

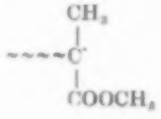
TABLE 1. CHARACTERISTIC HYPERFINE STRUCTURES OF THE SPECTRA OF MACRORADICALS

Polymer	Number of lines	Spacing between adjacent lines [gauss]	Method of obtaining the radicals*
Polystyrene	3	34	b
Low-pressure polyethylene	6	27	b
Polymethyl methacrylate	5	27	a, b
Polymethacrylic acid	5	27	a
Polyacrylic acid	3	29	a
Polymethyl acrylate	3	29	a, b
Polyisobutylene	7	29	b
Polyvinyl acetate	3	17	a, b
Thiokol	3	45	b
Polycaprolactam	3	40	b

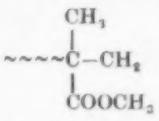
* (a) radicals trapped during polymerization, (b) radicals formed in mechanical disintegration.

The hyperfine separation is abnormally large in the case of thiokol. It is possible that anisotropic interactions take part in the formation of this spectrum; this was recorded in work [7] relating to the analogous spectrum of irradiated lanthionine.

The following fact also attracts attention. In the spectrum observed on the mechanical disintegration of poly-(methyl methacrylate) in liquid nitrogen, four intermediate weak lines observed in the polymerization of the monomer are absent. It is known from the literature [8] that these lines are absent in the polymer after irradiation at a low temperature. On warming to room temperature, however, the spectrum immediately and irreversibly assumes its normal form. This means that there is present in the polymer a certain amount of active radicals the spectrum of which does not appear in the region of the spectrum of the "normal" radicals



Reaction with the surrounding medium, into which the active radicals enter on defrosting, produces radicals with a quadruplet spectrum. The



radicals inevitably arising in the breaking of the polymer chains may represent these active radicals. The appearance of the satellite lines in the EPR spectrum during the polymerization of MMA and MAA can be explained by assuming the possibility of abnormal ("head to head") addition of monomer links in the process of building the polymer chain, which leads to the appearance of active macroradicals in this case also.

In itself, the nature of the radical giving the spectrum of four intermediate lines is still unclear. We have suggested that it is connected with a secondary effect—the transfer of the reaction centre to the unsaturated end of the chain [1]. However, further investigations of the kinetics of the formation and destruction of this secondary radical have not yet given clear results.

The phenomenon of the change in the spectrum of macroradicals has also been observed with methyl acrylate, where the triplet spectrum is gradually transformed into a singlet spectrum.

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SPIN-LATTICE RELAXATION TIME

It has proved to be possible to measure the spin-lattice relaxation time τ of macroradicals trapped in certain polymers with the aid of the apparatus described earlier [1]. The measurements were carried out by the saturation method, that is, the relaxation time was determined from the dependence of the intensity of absorption on the energy density of the electromagnetic field.

In accordance with the determination of the imaginary part of the magnetic susceptibility χ'', the losses in the resonator and, consequently, the intensity at the outlet of the amplifier system are proportional to the magnitude

$$U \sim \frac{d}{dH}\left[\int_V \frac{d\chi''}{dv} H_1^2 dV\right] \tag{1}$$

Here integration is carried out with respect to the volume of the specimen V: H_1 is the amplitude of the magnetic component of the electromagnetic field perpendicular to the stationary field H. It is assumed that recording of the derivative of the absorption with respect to the magnetic field takes place in the spectrometer, as usual.

For a cylindrical specimen of small diameter (2–3 mm) located along the axis of a cylindrical resonator of type H_{011}, it is possible, with satisfactory accuracy, to take H_1 as constant along a radius and as varying in accordance with a cosine law along the axis:

$$H_1 = H_{1m} \cdot \cos\frac{\pi z}{L}, \tag{2}$$

where z is the distance from the centre of the resonator along the axis; H_{1m} is the value of H_1 at the centre of the resonator; and L is the height of the resonator.

The dependence of χ'' on H_1 is given, as is known [9], by the equation:

$$X'' = X_0'' \cdot \frac{1}{1 + \frac{\pi^2 g \mu_0}{2h} \tau s(H) H_1^2} \tag{3}$$

where χ'' is the limiting value of χ'' for a small energy density of the field; g is the spectroscopic resolution factor; μ_0 is the Bohr magneton; h is Planck's constant; and $s(H)$ is a function defining the form of the absorption line and standardized such that

$$\int_0^\infty s(H)dH = 1. \tag{4}$$

Formula (1) together with (2) and (3) determines the dependence of the magnitude of the signal in the detector U on the saturation parameter

$$q = \frac{\pi^2 g \mu_0}{2h} H_{1m}^2 s(H_0)\tau \tag{5}$$

and on the magnetic field H.

Further, by taking into account the condition

$$\left[\frac{dU}{dH}\right]_{\max} = 0 \tag{6}$$

the dependence of the maximum signal $U_{\max}$ on q is determined. Curves have been constructed which express the dependence found theoretically by the given method between

$$\lg (U_{\max}/H_{1m}^2)$$

and $\lg q$ for the cases of the lorentzian and the gaussian form of the absorption line (Fig. 8). One of these curves coincided with that drawn to the same scale of the experimentally found dependence of $\lg (U/P) = f(\lg P)$ in such a way that the corresponding co-ordinate axes remained parallel to one another (P is the power of the ultra high frequency generator).

The point of intersection of the ordinate axis of the theoretical curve with the abscissa axis of the experimental curve makes it possible to determine the value of the power of the generator for which the parameter $q=1$. Knowing the value H_{1m} at the centre of the resonator at the given power, it is easy to calculate τ from equation (5). An example of a similar combination is given in Fig. 9 and the results of the measurements in Table 2.

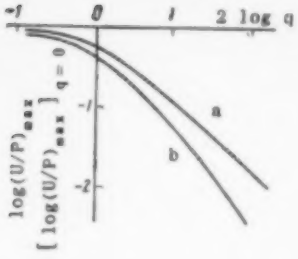

FIG. 8. Graph for the determination of relaxation times: (a) For a gaussian form of the absorption line: (b) For a lorentzian form.

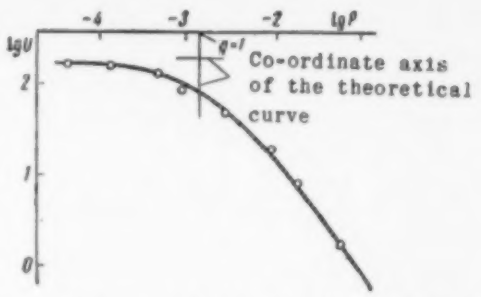

FIG. 9. Example of the determination of τ for the macroradicals of polymethacrylic acid at 20°. (P in watts, U in arbitrary units)

TABLE 2. RELAXATION TIMES OF EPR SPECTRA OF MACRORADICALS

Polymer	T,°K	τ, sec	Polymer	T,°K	τ, sec
Polymethyl methacrylate	77	$1{\cdot}0\times10^{-4}$	Polyacrylic acid	77	$>3\times10^{-3}$
,,	300	$1{\cdot}3\times10^{-4}$	,,	300	$2{\cdot}5\times10^{-4}$
,,	300	$1{\cdot}5\times10^{-4}$	Polymethyl acrylate	77	7×10^{-4}
Polymethacrylic acid	77	$1{\cdot}2\times10^{-4}$	,,	300	$1{\cdot}5\times10^{-4}$
,,	300	$1{\cdot}8\times10^{-4}$	Polyvinyl acetate	300	$\ll10^{-5}$
,,	408	$1{\cdot}2\times10^{-4}$	Racicals with the reaction centre on an oxygen atom	300	$\ll10^{-5}$

In favorable cases, the method makes it possible to determine τ relatively with an error of the order of ±50 per cent. In the determination of the absolute magnitude of τ, additional errors are introduced, connected with the measurement of the breadth and form of the absorption line and H_{1m}, so that only the order of magnitude of this quantity is determined.

Attention is drawn to the weak dependence of τ on the temperature in the case of methacrylate polymers and also on the nature of the hydrocarbon substituents.

At the same time, no saturation is observed for radicals of polyvinyl acetate at a level of the power of the generator of the order of tens of milliwatts and, consequently, τ for these is at least an order of magnitude lower. Thus the addition of oxygen directly to a radical carbon atom sharply decreases the spin-lattice relaxation time.

As regards macroradicals with a reaction centre on an oxygen atom, they also do not reveal any indication of saturation of the spectrum and, consequently, the relaxation time for them is less than 10^{-5}sec. The absence of any marked

temperature dependence of τ does not contradict current theories [10]. The nature of this magnitude is quite complex and further results must be accumulated in order to learn its interpretation.

CONCLUSIONS

The accumulation of "trapped" macroradicals even in the comparatively early stages of the homogeneous photopolymerization of vinyl acetate and methyl acrylate bears witness to the insufficiency of classical ideas concerning the kinetics of this process. Apparently "trapping" takes place of macroradicals of comparatively great size in which the reaction centre, if it is present in the interior of the tangled formation, may be difficult of access for the monomer.

Study of the kinetics of the destruction of macromolecules trapped in a polymer points to the diffusion character of this process.

The triplet hyperfine structure of the EPR spectra for the macroradicals of methyl acrylate, vinyl acetate and acrylic acid, and also the similarity of the spectra for methacrylic acid and methyl methacrylate, confirms the hypothesis of Ingram [3] that one of the β-protons of the methylene group does not interact with the unpaired electron.

The investigation which was carried out on macroradicals arising in the vicinity of the breakage in the mechanical disintegration of polymers made it possible to establish the nature of the electron paramagnetic resonance spectra of these radicals. The method was shown to be suitable in a series of cases for the detection of the "weak points" in a macromolecule chain at which breakage takes place. In particular, it was shown that in polystyrene and polyethylene these weak points are inclusions of oxygen in the covalent chain.

Translated by B. J. HAZZARD

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POLYMETHYLBUTOXYPHOSPHINEALUMOXANES*

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(*Received* 27 *June* 1959)

THE possibility of the formation of polymers having primary molecular chains consisting of aluminium and oxygen atoms with trialkylsiloxane substituents was shown earlier [1].

The possibility of synthesising organophosphorus aluminium compounds and their conversion into polymers having primary molecular chains consisting of aluminium and oxygen atoms, with methylbutoxyphosphinyl substituents is examined in the present work.

The synthesis of the organophosphorusaluminium compounds was achieved by the esterification of methylphosphinyl chloride with butanol and the subsequnt reaction of the methylbutoxyphosphinyl chloride obtained with aluminium butylate according to the following scheme:

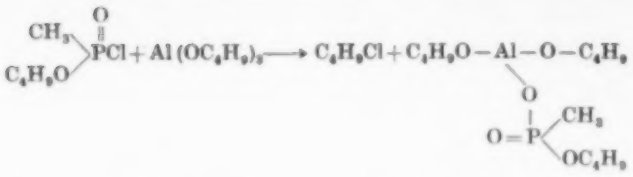
$$CH_3P(O)Cl_2 + C_4H_9OH \longrightarrow \begin{matrix} CH_3 \\ C_4H_9O \end{matrix}\!\!>\!P(O)Cl + HCl$$

$$\begin{matrix} CH_3 \\ 3C_4H_9O \end{matrix}\!\!>\!P(O)Cl + Al(OC_4H_9)_3 \longrightarrow 3C_4H_9Cl + \left[\begin{matrix} CH_3 \\ C_4H_9O \end{matrix}\!\!>\!P(O)-O \right]_3 Al$$

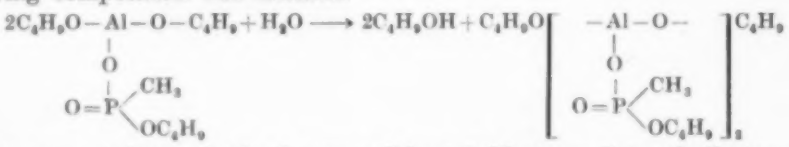
Methylbutoxyphosphinyl chloride was isolated in a pure form with a yield of 25·6 per cent of theory from the first reaction. In this synthesis a considerable residue is formed which consists of a product which is difficult to separate, probably dimethylbutoxypyrophosphate. The second reaction takes place readily at a temperature of 110–140° with the seperation of butyl chloride in a quantity approaching theoretical. As a result of the reaction tri- (methylbutoxyphosphine) aluminium is formed in a high yield.

The reaction takes place more readily with an equimolar ratio of methylbutoxyphosphinyl chloride to aluminium butylate with a complete substitution of its butoxy group and the separation of butyl chloride according to the reaction:

* Vysokomol. soedin. **1**: No. 9, 1390–1395, 1959.



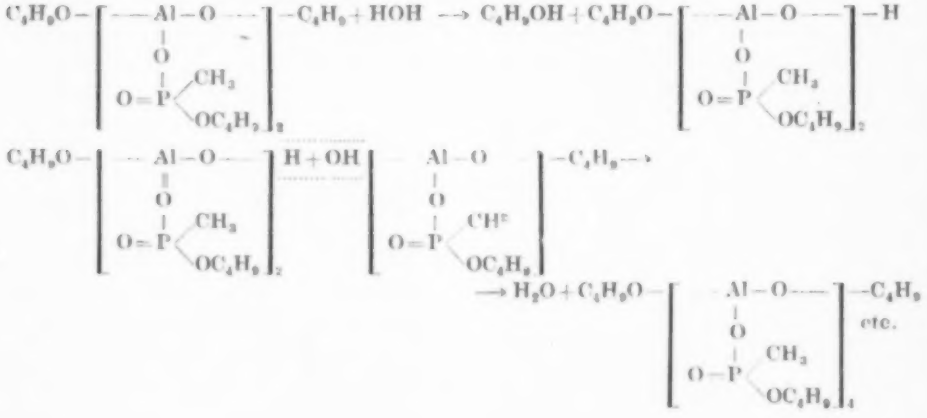
However, because of its great tendency to hydrolyse the isolation of pure methylbutoxyphosphine-dibutoxyaluminium was unsuccessful. A dimer of the following composition was isolated:



The new products obtained were solids: 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane dissolves in xylene, benzene, butyl and ethyl alcohols and does not dissolve in methyl alcohol; tri-(methylbutoxyphosphine)aluminium dissolves only in methyl alcohol. An investigation of the properties of these compounds showed that 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane is readily hydrolysed by water but that tri(methyl-butoxyphosphine)aluminium is stable against hydrolysis, even on heating.

In the action of water on 1,3-dibutoxy-di-(methylbutoxyphosphinealumo) oxane the butoxy groups attached to the aluminium atom undergo hydrolysis. Arising from this, an attempt was made to investigate in more detail the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo) oxane with the aim of synthesising by this method, polymers with primary molecular chains consisting of aluminium and oxygen atoms with methylbutoxyphosphinyl substituents.

The experiments showed that the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with water takes place with the seperation of butyl alcohol and is accompanied by an increase in the viscosity of the product of hydrolysis. This process probably proceeds according to the scheme:



In the investigation of the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane dissolved in xylene it was noted that on the addition of water-saturated butanol to the xylene solution the 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane solution thickens, but on standing or heating it gradually acquires a viscosity close to the original solution. Heating a xylene solution of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with water-saturated butanol at 120° leads to a gradual increase in the viscosity of the product which indicates not only hydrolysis but also a process of thickening in the product of hydrolysis. The increase in the viscosity of the solution of the hydrolysis product depends markedly on the amount of water used in the hydrolysis reaction and is higher the greater the amount of water used.

Experimental data obtained from the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with 1·0 and 2·0 moles of water are shown in Fig. 1.

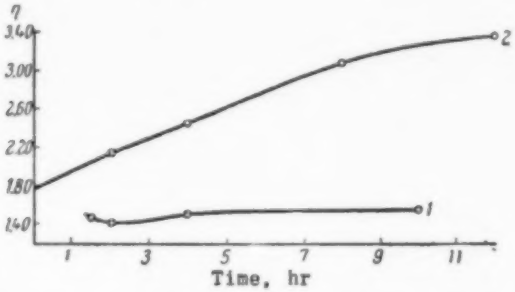


Fig. 1. Relative viscosity of a 10% solution of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane in a xylene-butanol mixture on hydrolysis: (1) 1·0 mole H_2O; (2) 2·0 moles H_2O.

The product was hydrolysed in xylene by aqueous butyl alcohol. It is seen from Fig. 1 that the viscosity of the solution is altered little in the hydrolysis with 1·0 mole of water but is considerably higher with 2·0 moles; however, the high increase in viscosity on hydrolysis with 2 moles is unimportant. This may be explained by the presence in solution and the formation during the reaction process of butyl alcohol which leads to a very early approach to equilibrium in the process of hydrolysis and condensation. Polymers isolated from solutions by vacuum stripping and subsequently dissolved again had a higher degree of viscosity which confirms such a conclusion. This is seen in the Table, where the viscosity is shown of the products of hydrolysing 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with different quantities of water before and after the removal of the solvent.

A particularly sharp increase in viscosity is observed in the reaction products obtained by the hydrolysis of 1,3-dibutoxy-di(methylbutoxyphosphinealumo) oxane with 1·5 and 2·0 moles of water. After removal of the solvent the hydrolysis product from the hydrolysis with 2·5 moles of water loses its solubility in xylene

but swells in it, increasing greatly in volume and dissolves only in a mixture of xylene or benzene with methyl alcohol. The viscosity of the polymer solution obtained by the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo) oxane with 2·0 moles of water increases about 10 times.

All the polymers obtained by the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane were isolated from solution by distilling off the solvent and were solid materials soluble in xylene and benzene. On applying the solutions to the surfaces of various materials and evaporation of the solvent they form solid, transparent, brittle films.

An investigation of the thermomechanical properties of the polymers obtained from xylene-butanol solutions showed that with an increased amount of water for the hydrolysis of 1,3-dibutoxy-(methylbutoxyphosphinealumo)oxane their temperature of vitrification T_v increased. T_v is about 50° for the polymer obtained by hydrolysis with 0·5 mole of water but it is higher than 150° for the polymer obtained by hydrolysis with 2·5 moles of water (see Fig. 2).

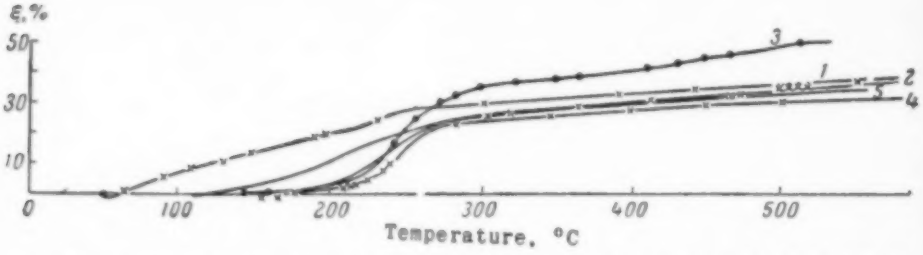


FIG. 2. Thermomechanical curves of the polymers obtained by the hydrolysis of 1,3-dibutoxydi-(methylbutoxyphosphinealumo) oxane. (1) 0·5; (2) 1·0; (3) 1·5; (4) 2·0 and (5) 2·5 moles $.H_2O$.

All the polymers investigated did not flow even at 650°. This shows that the polymers obtained had a very high melting point, higher than the range investigated. Such a characteristic in the thermomechanical curves is probably explained by formation of regular structure by the polymer during the heating process which, as shown in our experiments, is accompanied simultaneously by the loss of solubility of the polymer. This is confirmed by the soluble polymer losing its solubility after heating for 2 hr at 200°

EXPERIMENTAL

Methylbutoxyphosphinyl chloride. We put 39·76 g (0·3 mole) of methylphosphinyl chloride into a flask fitted with a stirrer, reflux condenser, dropping funnel, a thermometer and a capillary for bubbling nitrogen, added 40g of xylene and while mixing at +15–20° added drop-wise 0·3 mole of butyl alcohol. During the introduction of butyl alcohol, hydrogen chloride was evolved which was

removed by the stream of nitrogen. 13·13g of methylbutoxyphosphinyl chloride, B.P.78–79°/9mm, were obtained by vacuum distillation (25·6 per cent of theory).

Found %: C 35·15; H 7·36; Cl 20·69; P 17·59.
$C_5H_{12}POCl_2$ Calculated %: C 35·37; H 7·08; Cl 20·93; P 17·74.

Tri-(methylbutoxyphosphin)aluminium. The synthesis was carried out by two methods.

(1) 1·23g (0·005 mole) of aluminium butylate and 2·80g (0·015 mole) of methylbutoxyphosphinyl chloride were put into a two-necked flask fitted with a stirrer and a top for the collection of the butyl chloride which separates during the course of the reaction. On heating to 80° the mixture reacted rapidly with the separation of 1·41g (theoretical amount 1·47g) of butyl chloride. The tri-(methyl-butoxyphosphine)aluminium produced is a white solid which does not melt on heating to 650° and is soluble in methyl alcohol.

(2) We added drop-wise at 100° a solution of 4·90g (0.2 mole) of aluminium butylate in 20g xylene to 10·44g (0·06 mole) of methylbutoxyphoshinyl chloride placed in a flask, fitted with a stirrer and dropping funnel. The solid product obtained is soluble in methyl alcohol but insoluble in xylene and benzene. To isolate pure tri-(methylbutoxyphosphine)aluminium the product was dissolved in methyl alcohol, reprecipitated by water, washed with water, dried and analysed. The re-precipitated product dissolves in methyl alcohol.

Found %: C 38·14; H 7·60; P 19·34; Al 5·61.
$C_{15}H_{36}P_3AlO_3$ Calculated %: C37·53; H 7·50; P 18·85; Al 5·02.

1,3 Dibutoxy-di-(methylbutoxyphosphinealumo)oxane was obtained by method 2. We added 34·09g (0·2 mole) of methylbutoxyphosphinyl chloride dropwise at 110–140° to 49·27g (0·2 mole) of aluminium butylate dissolved in 150·2g xylene. 54·7g (a yield of 84·5 per cent of theory) of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane was obtained. This solid material dissolves readily in xylene, benzene and butanol but slightly in ethanol. The product is readily hydrolysed by moist air and water.

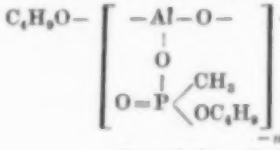
Found %: Al 11·02; 11·10; P 11·15; 11·41
$C_{16}H_{42}P_2H_2C_9$ Calculated: Al 10·41; P 11·96

Hydrolysis of 1,3 dibutoxy-di-(methylbutoxyphosphinealumo)oxane. We added water-saturated butyl alcohol to a xylene solution of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane in such a quantity as to yield with one mole of product 0·5; 1·0; 1·5; 2·0 and 2·5 moles of water. The viscosity of 10% solutions of the product prepared in this way was determined in which we placed the 10% solutions of the product into a round-bottomed flask fitted with a reflux condenser and a calcium chloride tube and heated it to 120°. Over fixed intervals of time we took samples and determined the relative viscosity at 20° of the 10% solutions of the polymer products in an Ostwald viscometer. The experimental data are shown in Fig. 1.

At the approach to equilibrium i.e. at the end of the reaction we placed the 10% solution of the product from hydrolysing 1,3 dibutoxy-di-(methylbutoxy-

phosphinealumo)oxane in a vacuum distillation apparatus and heated it to 120° in which according to the distillation of the solvent we gradually reduced the residual pressure of the system to 7 mm. A solid polymeric product with a slightly yellowish colour was obtained which dissolved in xylene and benzene.

The polymers obtained by the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with 1·0 and 1·5 moles water had fixed phosphorus and aluminium contents which correspond to



Found %: C 32·32; H 6·81; Al 12·42; P 15·15.
For $n=12$. Calculated %: C 33·22; H 6·59; Al 13·17; P 15·12.
Found %: Al 14·15; P 14·65.
For $n=24$. Calculated %: Al 13·52; P 15·53.

We dissolved 1g of the polymer product obtained after vacuum stripping in 9g xylene and determined the relative viscosity of the 10% solution obtained.

The thermomechanical properties of the polymers produced by the hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane with 0·5; 1·0; 1·5; 2·0 and 2·5 moles water were investigated by methods described earlier [2].

In conclusion the authors wish to express their appreciation for the obliging aid given by colleagues at the G. L. Slonimskii laboratory in recording the thermomechanical curves of the polymers.

CONCLUSIONS

(1) Methylbutoxyphosphinyl chloride, tri-methylbutoxyphosphine)aluminium and 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane are synthesised.

(2) The hydrolysis of 1,3-dibutoxy-di-(methylbutoxyphosphinealumo)oxane is investigated and it is shown that it readily forms polymeric materials which are soluble in organic solvents. Solutions of the polymers applied to the surface of a solid form clear, solid, brittle films after evaporation of the solvent. The thermomechanical properties of the polymers obtained are investigated and it is found that the vitrification temperature rises with increased amounts of water used for the hydrolysis reaction. The polymers obtained had vitrification temperatures of 50–150° but showed no fluidity at 650°.

(3) On heating the polymers readily undergo modifications which are accompanied by a loss of solubility.

Translated by R. G. P. TOWNDROW

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CRYSTALLINE POLYVINYL CHLORIDE*

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(*Received* 3 *July* 1959)

The discovery of new methods of polymerizing olefines enabled a number of polymers possessing regular structural chains and capable of being easily crystallized, to be obtained for the first time and their properties studied. [1–5]

The production of crystalline polyvinyl chloride from tetrahydrofuran at 30° in the presence of a heterogeneous catalytic system consisting of a mixture of tri-*iso*-butylaluminium and vanadium trichloride recently became known [6]. It was noted that it was possible to obtain polyvinyl chloride having a crystalline type of X-ray diffraction pattern in the presence of triethylaluminium, ethers and vanadium compounds. A polyvinyl chloride fraction recrystallised from boiling *cyclo*hexanone with methyl alcohol had a specific viscosity of 0·15 (a solution in *cyclo*hexanone at 135°) and contained 54·9 per cent of chlorine on analysis.

Crystalline polyvinyl chloride was obtained by us in the presence of a common heterogeneous catalytic system consisting of a mixture of trialkylaluminium and titanium trichloride in a medium of saturated hydrocarbons with certain complex-forming additives (sulphuric ether, dioxane, amines) which obviously contribute to the formation of more stable complexes with the oxygen or nitrogen atoms on the catalytic solid surface. The experiments were carried out at 45–70° in metal reactors of 4 l. capacity provided with a stirrer (180 rev/min) and a thermostat [7].

The results of certain typical experiments are set out in Table 1.

Each time the polymer was obtained in the form of a finely dispersed powder containing a fraction insoluble in *cyclo*hexanone; the polymer contained 53–54 per cent chlorine. The colour of the powder obviously depended on the nature of the complex formed on mixing the ether or amine with the titanium trichloride and triethylaluminium. The original hypothesis that the possible course of the dehydrochlorination reaction is parallel with the synthesis of polymers under the influence of metals which catalyse this reaction was not confirmed, since HCl was not found in the mother liquor or in the gases evolved. As the usual methods of washing did not succeed and because of the presence of the insoluble fraction, a polyvinyl chloride fraction having a constant (0·9–0·11) specific viscosity in (*cyclo*hexanone at 20°) independent of the composition of the catalytic system and containing 55·58 per cent chlorine on analysis, was isolated by extraction with

* Vysokomol. soedin. 1: No. 9, 1403–1406, 1959.

TABLE 1. POLYMERIZATION OF VINYL CHLORIDE IN THE PRESENCE OF ORGANO-METALLIC COMPLEXES

Vinyl chloride (g)	Solvent (g)	Complex-forming additive (g)	Amount of titanium-trichloride (g)	Amount of triethylaluminium (g)	Reaction temperature (°C)	Duration of reaction (hr)	Yield of polymer (g)	Colour of product on recrystallization
400	*n*-heptane (70)	diethyl ether (430)	1·7	2·7	45 and 70	6·13	2·5	Black
452	benzine (306))	diethyl ether (194)	45·2	68·0	45 and 70	18·22	268	Grey
452	benzine (306)	diphenylamine (4)	45·2	68·0	45 and 70	18·22	230	Pink
452	*n*-heptane (306)	diphenylamine (4)	45·2	68·0	45 and 70	18·22	185	Coffee-coloured
452	benzine (306)	triethylamine (2·5)	45·2	68·0	45 and 70	18·22	55	Coffee-coloured
452	benzine (306)	—	45·2	68·0	45 and 70	18·22	69	Grey-green

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*cyclo*hexanone and precipitation of the dissolved polymer by the addition of methyl, alcohol, in order to avoid the coloration of the polymer and to study it in a sufficiently purified state.

The polyvinyl chloride obtained possessed a sufficiently high dissociation temperature (of the order of 180–190° by Congo Red) some 30–40° higher than its melting point 135–150°). Thus, in the molten state the polymer is able to preserve its structure for a certain period with little chemical change. Its thermostability seemed to be twice as high as the thermostability of a commercial sample (15 min against 7) which is apparent from Fig. 1 (the kinetics of the dehydrochlorination of polyvinyl chloride carried out at 175° in an atmosphere of oxygen).

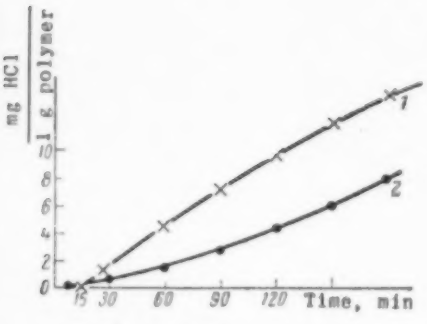

FIG. 1. Dehydrochlorination of polyvinyl chloride; (1) Crystalline polymer; (2) Commercial sample.

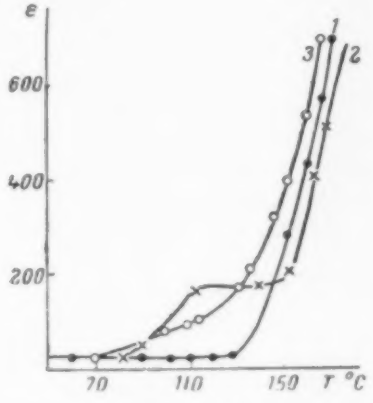

FIG. 2. Thermomechanical curves: (1) Crystalline polymer (2) "Amorphized polymer; (3) Commercial sample.

It must be noted, however, that the velocity of dehydrochlorination of this sample was higher than the velocity of dehydrochlorination of the ordinary commercial polymer which is produced by the radical polymerization method. This effect may have resulted from a difference in the structure of the polymer chain and the presence of traces of metal compounds in the polyvinyl chloride under investigation which participated in the stereosynthesis of the polymer and catalysed the dehydrochlorination reaction.

The precipitated polyvinyl chloride was subjected to thermomechanical testing on a Kargin dynamometric balance. The samples were prepared in the form of tablets 10 mm in diameter and 5 mm in thickness by pressing in a laboratory press.

The results of the thermomechanical testing are presented in Fig. 2. The precipitation temperatures are along the abscissae axis and the amount of deformation of the tablets under constant load are along the ordinate axis. The thermomechanical curve is characteristic for a crystalline polymer and differs from the

industrial sample of polyvinyl chloride (curve 3) produced by the usual radical polymerization method. The sample under investigation remained practically undeformed under the conditions of testing and melted over a narrow range of temperature, of the order of 135°, changing into a viscous-fluid state. At a temperature of the order of 80° the conversion into the highly elastic state was more noticeable with an "amorphized"* sample (curve 2). The third sample, also amorphous (curve 3), changed into the highly elastic state practically at the temperature of vitrification although it did not have an extended range for the softening point but melted over a narrow range of temperature.

On the basis of the results of the thermomechanical tests the conclusion may be drawn that the precipitated polyvinyl chloride is a new example (together with isotactic polystyrene and polyethylene terephthalate) of a crystallizable plastic whose region of vitrification is higher than room temperature.

The ability of the polyvinyl chloride under investigation to crystallize during the initial heating above the temperature of vitrification is confirmed by electronographical investigations. The electronograms were obtained by the method of passing a beam of electrons through the sample. We prepared polyvinyl chloride films at room temperature on a collodion base from a solution of the polymer in *cyclo*hexanone by evaporating the solvent from a water surface.

The electronograms of the "amorphized" films (Fig. 3a) had the appearance of three hollow rings, the maximum darkening of which corresponded to the following inter-plane distances: 1–5·27 A; 2–3·65 A; 3–2·31 A. The same film heated for 2·5 hr at 135° and slowly cooled in the thermostat to room temperature gave a diffraction pattern in the form of ten hollow rings with $d=5{\cdot}27$, 5·08, 4·63, 3·65, 2·85, 2·31, 2·26, 2·06, 1·83 and 1·69 Å (Fig. 3b). As a comparison of the degree of order of the polyvinyl chloride produced by us with the usual material, diffraction patterns were obtained with the latter which were analogous with those obtained in earlier work [9]. Consequently, Fig. 3c and 3d show electronograms of a film of ordinary polyvinyl chloride produced at room temperature and the same film heated for 2·5 hr at 135° and slowly cooled to room temperature in a thermostat. As is evident from Fig. 3a and 3c the electronogram of the unheated amorphous film has reflections corresponding to the same inter-plane distances which are also in the "amorphized" film of crystalline polyvinyl chloride although with less sharp boundaries. Four soft rings with $d=5{\cdot}27$, 4·63, 3·65 and 2·31 Å. can be seen on the electronogram of the ordinary polyvinyl chloride heated to 135° (Fig. 3d).

On the electronogram of the crystalline polyvinyl chloride these reflections become considerably sharper (Fig. 3b) and, as noted above, new reflections appear corresponding to inter-plane distances of 5·08, 2·85, 2·26, 1·83 and 1·69 Å. This indicates the appaerance of new elements of order due to crystallization occurring in the sample. The ability of the polymer to crystallize is apparently dependent

* Amorphous sample prepared from crystalline product.

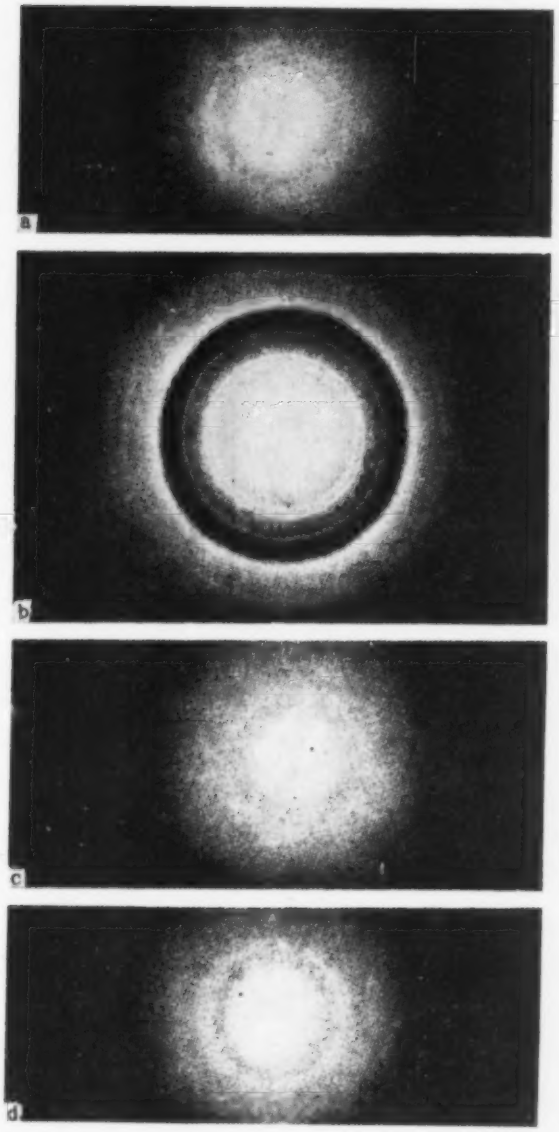

FIG. 3. Electron diffraction photographs of polyvinyl chloride: (a) crystalline; (b) Crystalline, heated for 2·5 hr at 135°; (c) Commercial sample, unheated; (d) The same, heated for 2·5 hr at 135°.

on the high regularity of its chain in the sense of correct alternation of the asymmetrical carbon atoms along the chain.

The correspondence of the four reflections appearing in the electronogram of the commercial sample of polyvinyl chloride with four of the ten reflections appearing with the crystallized sample under investigation indicates that the structure of the amorphous polymer produced by the radical polymerization method contains ordered elements which recur in the crystalline sample. Similar observations can readily be interpreted on the basis of a model of the structure of crystalline and amorphous polymers proposed by Kargin, Kitaigorodskii and Slonimskii.[8] According to this model the crystalline and amorphous polymers consist of bundles of parallel chains. The bundle of the crystalline polymer differs from the bundle in the amorphous polymer in that in the former there exists an azimuthal order in the distribution of the side groups. The regularity in the amorphous bundle can vary within broad limits and in a series of cases approximates to that in the crystalline polymer. A break in the structure of the chain of the radical polyvinyl chloride prevents the formation of the strictly azimuthal regularity inside the bundle and consequently prevents crystallization. The use of special conditions of synthesis in the present work obviously allowed this breaking to be eliminated and the crystalline polymer to be prepared.

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CONCLUSIONS

Polyvinyl chloride which gives diffraction patterns characteristic of crystalline polymers is synthesised by the polymerization of vinyl chloride in the presence of organometallic complexes.

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MECHANISM OF ION EXCHANGE ON CARBOXYL CATION EXCHANGERS*

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(*Received* 8 *July* 1959)

THE exchange of ions on carboxyl cation exchangers in which large organic cations take part has specific regularities in comparison with the simplest case of exchange, H^+–Me^+ or Me_1^+–Me_2^+. The retardation of the diffusion of an organic cation in a resin particle with the passage of time and the complete cessation of this process, lead to an irregular distribution of cations along the radius of the resin particle. The characteristics of a similar ionic exchange were demonstrated by us at length from the point of view of the existence of false states of equilibrium in such systems [1, 2, 3]. First of all these phenomena were studied during the exchange of streptomycin (Str, ionic weight = 584) on carboxyl cation exchangers in the hydrogen and salt forms. It was indicated in the results of further work that analogous conditions also occur in the exchange of other antibiotics (erythromycin and polymyxin which are also of a basic nature).

Methods of obtaining fine sections of resin particles and subsequent microphotographing of these sections were developed in our laboratary by Gerasimov, Bruns and Iakhontova. By carrying out the ionic exchange of coloured cations, dyed and used in these methods, Gerasimov succeeded in obtaining immediate visual confirmation of the uneven distribution of cations along the radius of the particles in the case of false equilibrium being established in the system.

The characteristics of the sorption of organic ions and the transition from true to false equilibrium with changes in the degree of swelling of the resins may be demonstrated by exchange on carboxyl cation exchangers in the hydrogen form. Carboxyl resins are slightly-dissociated polyelectrolytes and exchange on the hydrogen forms of these resins takes place considerably more slowly than on their salt forms, or on sulpho-cation exchangers in the hydrogen form [4]. A number of works are concerned with the study of the kinetics of the exchange of inorganic ions on the hydrogen form of carboxyl resins [4–7]. Generally, in all of these works the authors combine a slow exchange process with a low degree of ionization in the carboxyl groups of these cation exchangers. One of the prevailing points of view is that the diffusion of hydrogen ions from the resin appears to be the slowest stage of an exchange. Owing to a small degree

* Vysokomol. soedin. 1: No. 9, 1416–1421, 1959.

of ionization of the carboxyl group the concentration of H-ions in the resin particle is low, which leads to a low H-ion diffusion velocity from the cation exchanger and therefore a slow exchange. The Na^+–H^+ exchange is discussed in great detail in the work of Conway *et al.* [5]. In spite of the slow process of this exchange, however, a substitution of hydrogen by sodium takes place which corresponds to the equilibrium value of the resin capacity at a given pH of the solution.

For the majority of organic cations the stage which determines the exchange velocity also appears to be diffusion in the grains of the resin but during such an exchange even more complex conditions develop because of the diffusion of its own organic ions in the resin particle. This takes place more slowly than the diffusion of hydrogen ions from the resin. Owing to the necessity for maintaining the electroneutrality of the exchange a corresponding retardation of the diffusion of H-ions from the resin occurs and the limiting stage of the exchange becomes the diffusion of the organic ions in the cation exchanger particle.

In comparing the exchange of Na^+ and organic cations on carboxyl resins in the hydrogen form, it is necessary to emphasise two important points which have great significance in revealing the regular sorption of these and other ions. In the first instance, the exchange velocity of the organic cations and Na^+ in the initial period are very different and in the second, during the sorption of organic cations, incomplete use of the static exchange capacity (SEC) occurs in the exchange on cation exchangers, with an average and lower degree of swelling. These characteristics of the exchange of organic cations enable the role of separate factors in similar processes to be shown.

A comparison of the curves of the kinetics of the sorption of Na^+ and Str^{3+} sorbed from neutral solutions of known ionic strength [μ] in the presence of an OH anion exchanger, shows that the processes take place at different velocities and the amount of sorbed Na^+ exceeds the amount of Str^{3+} sorbed by 17 times (Fig. 1).

The data obtained show that for these processes the slowest stages of the exchange are different. If the velocity of the process is determined by the diffusion of H-ions from the resin in the case of the Na^+–H^+ exchange, then for Str^{3+}–H^+ the diffusion of the organic ion itself in the resin particle becomes the limiting stage. In this case a qualitative change in the structure of the resin is produced as a result of which a retardation of diffusion occurs. It must be noted that the sorption of Str^{3+} on the H form of the cation exchanger takes place over some 10 hr after which practically no increase in sorption is observed over a very long time (800 hr). Hence, it evidently follows that the coefficient of diffusion of Str^{3+} decreases to something of the order of the coefficient occurring in the initial period of the ion exchange process.

The course of the sorption of streptomycin with time for cation exchangers having different granulation, also indicates an essential difference in these processes from the kinetics of the Na^+–H^+ exchange. In the exchange of both

Na^+ and Str^{3+}, the exchange velocity depends on the granulation but at the end the amount of sodium sorbed is identical. In the Str^{3+}–H^+ exchange the final amount of Str^{3+} sorbed is different (Fig. 2). The data from the results

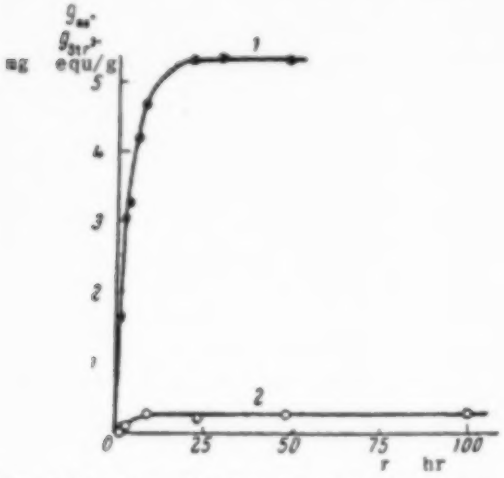

FIG. 1. Sorption of Na^+ and Str^{3+} on the H form of KFU cation exchanger; particle size 0·25–0·50 mm = 0·065; (*g*) amount of cations adsorbed in mg equ./g; (τ) time (1) Na^+; (2) Str^{3+}.

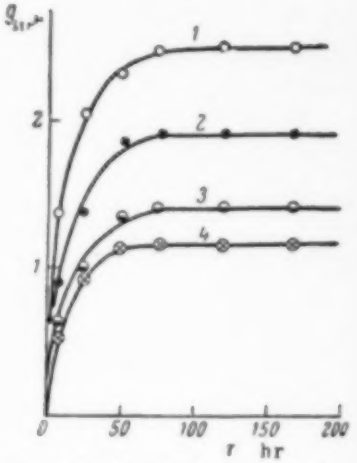

FIG. 2. Str^{3+} sorbed on the H form of KB-4 type of cation exchanger (9% DVB) in relation to resin granulation. (1) 0·03–0·06 mm; (2) 0·08–0·1 mm; (3) 0·25–0·55 mm; (4) 0·50–1·0 mm.

also confirm that in these cases the process does not retard the diffusion of H-ions from the resin. It is particularly interesting to trace the kinetics of the exchange of organic ions on a series of cations with varying degrees of swelling. They all possess a similar SEC for Na^+, but the amount of Str^{3+} ions sorbed by them sharply distinguishes one from the other (Fig. 3). On inspection these experiments allow the effect of varying resin structure on the sorption of organic ions to be demonstrated.

Under the most favourable conditions for the penetration of cations in the interior of the particle i.e. during sorption on a strongly swollen cation exchanger, the capacity for Na^+ and Str^{3+} coincides (Fig. 4), but in this case the velocity of Str^{3+} sorption is considerably lower than the velocity of Na^+ soption.

The difference in the mechanism of exchange appears particularly sharply in the sorption of Na^+ and organic cations from solutions of their bases. If it is assumed that the neutralization of the exchanging hydrogen ions proceeds immediately in the resin particle under these conditions, then the limiting effect of the diffusion of these ions from the cation exchanger particle must disappear. A sharp increase in the velocity of Na^+ exchange in the alkaline range compared with the neutral region, indicates the penetration of the alkali in

the resin particle, but the velocity of an exchange on carboxyl resins in the alkaline range remain lower in comparison with a similar exchange on sulphocation exchangers. In the case of Str^{3+} exchange with hydrogen ions of a cation

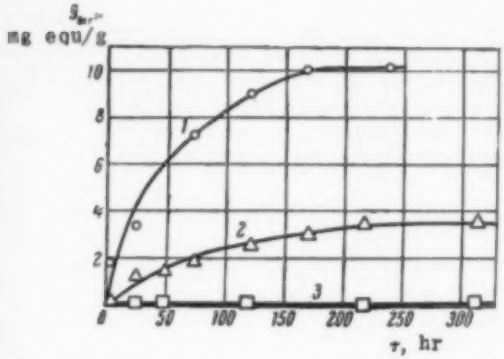

FIG. 3. Sorption of Str^{3+} by the H form of KB-4 type of cation exchanger possessing different swelling properties; particle size equals 0·5–1·0 mm. Coefficient expressed in the form of a relationship of the specific volume of the sodium form to the hydrogen form of the resin in the swollen state (1) $K=1·9$; (2) $K=1·7$; (3) $K=1·3$.

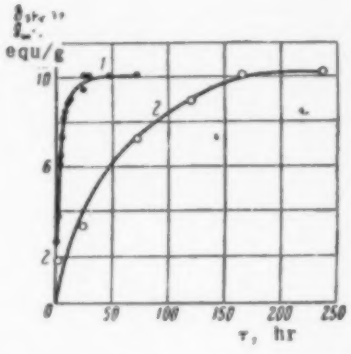

FIG. 4. Sorption of Str^{3+} and Na^+ on the H form of a highly swollen KB-4 type of cation exchanger (sample No. I); particle equals 0·5–1·0 mm; = 0·065; (1) Na^+; (2) STr^{3+}.

exchanger, the exchange proceeds very poorly in spite of the appearance of dissociated compounds in the streptomycin base having pK equal to 12; 12; 7·8 [8] [9]. This fact also confirms that in the case of Str^{3+} sorption the retardation of the exchange causes no diffusion of H-ions from the resin. Analogous results are also obtained for the sorption of polymyxin base. All the experiments written on the sorption of organic ions provide a basis for describing the general picture of the course of the ion exchange process, as with the sorption of ions the outer layers of the resin particles are filled by them. These layers are not very permeable and prevent further penetration of the organic ions into the particle which also leads to the cessation of sorption and the establishment of a false equilibrium.

The introduction of inorganic salts into a similar system cause the formation of a mixed form of resin (organic cation Na^+) in the outer layers of the particle. The permeability of the resin increases which involves a sharp increase in the sorption velocity and the amount of sorbed organic cations [9]. The part of Na^+ is shown particularly clearly during the sorption of Str^{3+} from solutions having the same ionic strength but containing Na^+ in different concentration. It is seen in Fig. 5 that the velocity of Str^{3+} sorption increases with an increase of Na^+ concentration.

Completely different phenomena occur in the system found in the true state of equilibrium before the addition of Na^+ (Fig. 6). In this case the displacement of Str^{3+} from the resin occurs on the addition of Na^+ to the system. This takes place in spite of the fact that under the conditions of the experiment

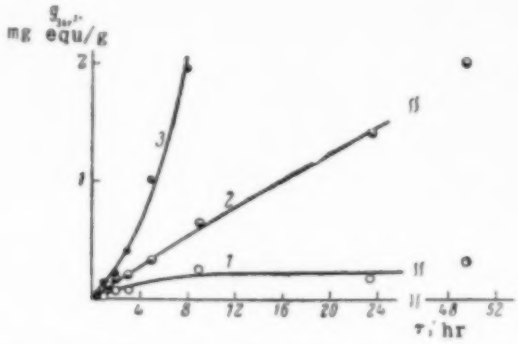

FIG. 5. Sorption of Str^{3+} on the original H-form of a KFU cation exchanger at constant μ(0·065) and different concentrations of Str^{3+} and Na^+; particle size 0·25–0·50 mm: (1) In the presence of Na_2SO_4; (2) 0·01 N·$=Na_2SO_4$; (3) 0·02 N·$=Na_2SO_4$.

an increase in the ionic strength of the solution is observed which, as was shown, can cause an increase in the capacity of the cation exchanger agreeing with the potentiometric titration curves for a given resin. Every combination of these experiments shows conclusively that the part of Na^+ consists of varying the

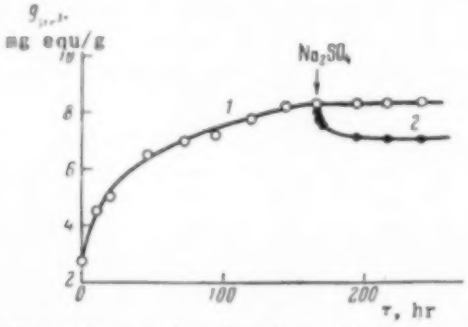

FIG. 6. Action of Na^+ on the sorption of Str^{3+} by the H-form of a highly swollen KB-4P-7 cation exchanger; particle size 0·5–1·0 mm: (1) Sorption of Str^{3+} on the H-form of a resin; (2) Sorption of Str^{3+} after addition of 0·3 N·$=Na_2SO_4$.

composition and structure of the external layers of the cation exchanger particle. In this way conditions are created which facilitate the diffusion of Str^{3+} into the particle.

An investigation of the sorption of Str^{3+} from neutral solutions on to the original H-forms of the carboxyl cation exchangers in the presence of Na^+ in

solution and the use of different methods for removing the H-ions displaced from the cation exchangers [10–11] enables an approach to be made to the solution of the problem of the mechanism of ion exchange on cation exchangers with different degrees of swelling. Fig. 7 shows that for each resin the final quantity of sorbed Str^{3+} is identical and independent of the method of removing H-ions from the system. This means that the state of such a system determines

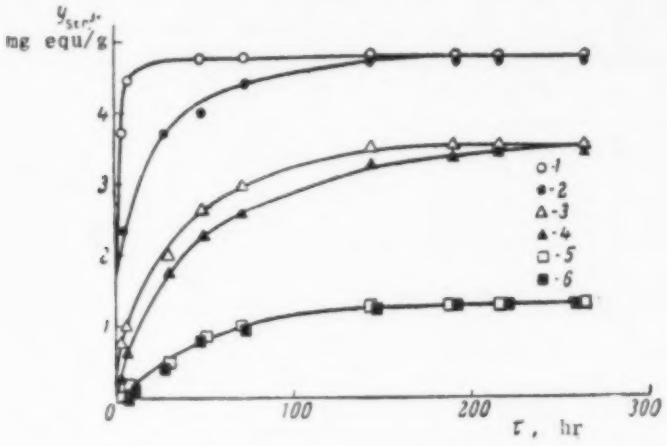

FIG. 7. Sorption of Str^{3+} by the original H-forms of KB-4 type cation exchangers in the presence of a phosphate buffer (I) or Na_2SO_4 and an OH-anion exchanger (II). Na^+ concentration—0·45 N; pH 7, particle size d=0·5–1·0 mm (1) I; (2) II K_{swell}=1·9; (3) I; (4) II, K_{swell}=1·5; (5) I; (6) II, K_{swell}=1·3.

the concentration of Na^+ in it. However, the kinetics of the exchange in the presence of an anion exchanger or a phosphate buffer depend on the degree of swelling in the resin. Thus, for highly swollen cation exchangers, the sorption velocity with the introduction of a phosphate buffer is higher than that in the presence of sodium sulphate and an anion exchanger in the OH form. With a decrease in the swelling of a resin the exchange velocities become close and then identical. It is natural to suppose that in the case of exchange on a highly swollen resin, penetration of sodium phosphate into the cation exchanger particle and immediate neutralisation of the H-ions in the particle occurs. Therefore in the presence of a phosphate buffer, the exchange velocity is considerably higher than in the presence of sodium sulphate and an anion exchanger. With an increase in the amount of divinylbenzene the structure of the resin becomes more compact. For these cation exchangers the conditions for the removal of hydrogen ions by phosphate and an anion exchanger are approximately similar because neutralization of the H-ions occurs in solution.

CONCLUSIONS

The process of ion exchange on carboxyl cation exchangers in the hydrogen form in which large organic cations participate, is discussed. The sorption of such ions takes place considerably slower than the sorption of Na^+ ions owing to the slow diffusion of the organic cation itself in the resin particle. As the organic ions penetrate into the exchanger particle with a mean number of cross-links, a qualitative change in the resin structure takes place leading to a slowing down of the process and almost complete cessation of exchange. Under these conditions the number of sorbed organic cations per unit weight of resin is considerably less than the sxchange capacity of the cation exchanger at a given pH value of the solution.

Translated by R. G. P. TOWNDROW

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ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* VOL. 1. NO. 7, 1959*

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ON THE SYNTHESIS AND POLYMERIZATION OF GLYCIDYLURETHANES

A. A. Berlin and A. K. Dabagova, Vysokomol. soedin. **1**: No. 7, 946–950, 1959.

REPRESENTATIVES of a new class of monomers containing urethane and epoxy groups in the molecule (glycidylurethane) have been synthesized and described, Glycidylurethanes have been shown to polymerize at elevated temperatures to form insoluble, non-melting, vitreous products.

Glycidylurethanes are capable of copolymerization with organic compounds containing groups with reactive hydrogen (acids, phenols, alcohols).

It has been found that copolymerization of glycidylurethanes on metal and glass surfaces produces hard, strong, benzene-and oil-resistant films with high adhesion to the backing.

Glycidylurethanes are heat and light proofing agents for chlorine-containing polymers.

ON THE CONDENSATION TELEMERIZATION AND SYNTHESIS OF A NEW TYPE OF UNSATURATED POLYESTERS

A. A. Berlin, G. L. Popova and E. F. Isaeva, Vysokomol. soedin. **1**: No. 7 951–956, 1959.

IT has been shown that control of chain growth in polyesterification may be used to direct the synthesis of oligomeric polyesters containing reactive end groups. Utilizing methacrylic (or acrylic) acid as regulator of the polyesterification process, polyesteracrylates, representatives of a new class of unsaturated polyesters capable of polymerization, have been synthesized and described.

POLYMERIZATION OF MIXED POLYESTERS OF THE ACRYLIC SERIES AND PROPERTIES OF THE POLYMERS

A. A. Berlin, G. L. Popova and E. F. Isaeva. Vysokomol. soedin. **1**: No. 7, 957–961, 1959.

A STUDY has been made of the relation between the structure and number of acrylic groups of some types of polyesteracrylates (PEA), of their capacity for tri-dimensional polymerization and of the basic properties of the vitreous polymers formed. The presence of four acrylic groups in the PEA molecule has been shown to cause their hardening at 20° by benzoyl peroxide even in the absence of activators (dimethylal-anine, siccatives). Increase in the inter-double-bond distances in tetrafunctional PEA lowers the bulk contraction during polymerization to 0·6–2 per cent, and raises the specific impact viscosity and hardness of the polymers. Fields for the practical utilization of PEA as binders, adhesives, compoundings, coatings, pastes, etc. have been discussed.

* English Abstracts reprinted from Vysokomol. soedin. **1**: No. 7, 1959.

SYNTHESIS, POLYMERIZATION AND ADHESIVE PROPERTIES OF COPOLYMERS OF UNSATURATED GLYCIDOL ESTERS

A. A. Berlin, G. L. Popova and T. A. Makarova, Vysokomol. soedin. **1**: No. 7, 962–965, 1959.

GLYCIDYL METHACRYLATE (I), glycidyl acrylate (II), allyglycidyl carbonate (III) and allyglycidyl ether (IV) have been synthesized and investigated. It has been shown that in the presence of mineral acids and alkalis polymerization takes place owing to rupture of the ethylene oxide ring, viscous liquid polymers containing double bonds in the side chains being formed. In contrast to IV polymers I–III were shown to convert to tri-dimensional, vitreous products in the presence of benzoyl peroxide. Copolymers of I and butylmethacrylate have been obtained. Coatings on the basis of such copolymers were shown to possess considerable elasticity and strong adhesion to metallic surfaces.

EFFECT OF TEMPERATURE AND DEGREE OF CROSS LINKAGE ON THE FRICTIONAL PROPERTIES OF ELASTOMERS OF THE TYPE OF RUBBER

G. M. Bartenev and Z. E. Styran, Vysokomol. soedin. **1**: No. 7, 978–989, 1959.

THE results are presented of an investigation into the effect of temperature, slip velocity, type of rubber hydrocarbon and equilibrium modulus of the vulcanized rubber on the frictional properties of elastomers. It follows from the results presented that external friction of elastomers is a molecular-kinetic process connected with passage through energy barriers under the influence of thermal motion and external force of chains interlinked with the solid surface.

The theory of rubber friction is in harmony with the relations obtained.

SOME MECHANICAL PROPERTIES OF BF-4 POLYMER FILMS

A. L. Rabinovich, Vysokomol. soedin. **1**: No. 7, 998–1015, 1959.

IN the work the results are presented of elongation tests of BF-4 films from 3 to 160μ thick. The dependence of the elasticity modulus and films strength on the thickness was determined experimentally. The strained and stressed states of the films were studied under different conditions of stretch, namely, constant stretch velocity, constant stress and in the case of after-effects. A comparison has been made between the experimental data and the analytical expressions derived from the generalized Maxwell equation with account of elastic after-effects. The possibility has been examined of an analytic description of various conditions of isothermal uniaxal stretch on the basis of the above equation only containing four constants. It is intended do use the characteristics of BF-4 resulting from the study to develop a rational procedure for determining the mechanical properties of other polymers of this type and also for an approximate theoretical analysis of the deformations of vitreous plastics.

STUDY OF CRYSTALLIZATION CAPACITY OF SKI VULCANIZATES BY THE ADIABATIC STRETCHING METHOD

M. P. Votinov, S.A. Subbotin, V. V. Samoletova, S. P. Kopytovskaia and E. V. Kuvshinsky, Vysokomol. soedin. **1**: No. 7, 1016–1020, 1959.

THE basic relationships in the conversion of work to heat during the adiabatic stretching of unfilled lithium-isoprene rubber (SKI) have been investigated. The rubber specimens differed in molecular weight of the raw rubber and in the conditions of vulcanization. SKI vulcanizates of intrinsic viscosity $[\eta]=1{\cdot}8$ have been shown to remain amorphous on being

stretched to $\lambda \sim 10{\cdot}8$, whereas rubber of higher molecular weight ($[\eta = 4{\cdot}7$) begins to crystallize at $\lambda \sim 7$. The extent of crystallization of SKI is less than that of natural rubber in a mixture of the same composition. Natural rubber begins to crystallize at considerably lower elongations ($\lambda \sim 3$).

SYNTHESIS AND POLYMERIZATION OF *p*-TRIETHYLPLUMBYL-α-METHYLSTYRENE

V. V. Korshak, A. M. Poliakova and E. S. Tambovtseva, Vysokomol. soedin. **1**: No. 7, 1021–1023, 1959.

p-Triethylplumbyl-α-methylstyrene has been synthesized and its polymerization investigated. The polymer has been isolated. Its thermomechanical properties and intrinsic viscosity have been determined.

CONCERNING COPOLYMERIZATION WITH THE PARTICIPATION OF BIFUNCTIONAL MONOMERS

L. B. Sokolov and A. D. Abkin, Vysokomol. soedin. **1**: No. 7, 1024–1026, 1959.

A NUMBER of correlations in the formation of insoluble network polymers in the copolymerization of glycol di-α-chloroacrylate and methylacrylate, methylmethacrylate and styrene have been investigated. The factors determining the formation of insoluble copolymers during copolymerization with participation of a bifunctional monomer have been considered.

AN INVESTIGATION INTO THE MACROMOLECULAR PACKING DENSITY OF VARIOUS NATURAL CELLULOSE PREPARATIONS

V. I. Sharkov and V. P. Levanova, Vysokomol. soedin. **1**: No. 7, 1027–1033, 1959.

THE supermolecular structure of various types of natural cellulose, namely, bacterial, isolated from the wood of the fir tree and the bast fibres of flax, hemp, jute and ramie, has been studied by following the changes in residue density on alcoholysis and hydrolysis. The supermolecular structure of all the above types have been shown to differ from that of cotton cellulose. All the celluloses have been divided into three groups based on the shape of the residue density curves during ethanolysis, namely, the density (a) increases to a limiting value, (b) diminishes and (c) passes through a maximum.

It has been shown that fir and ramie cellulose in contrast to cotton cellulose do not change the shape of the ethanolysis density curves during mercerization.

On dry grinding wood cellulose assumes properties similar to ground cotton cellulose.

AN INVESTIGATION INTO THE SUPERMOLECULAR STRUCTURE OF CELLULOSE HYDRATE FIBRES

V. I. Sharkov and V. P. Levanova, Vysokomol. soedin 1: No. 7, 1034–1041, 1959.

To study the supermolecular structure of cellulose hydrate fibres, a method was employed based on measuring the rate of ethanolysis of the cellulose and the change in its specific gravity in the course of dissolution.

It has been shown that in the initial stages of ethanolysis considerable packing of the cellulose to a definite ultimate specific gravity is observed. The latter fluctuates with various fibres from 1·528 to 1·545. The initial specific gravity of extra-strong cellulose hydrate fibres was found to be less than that of ordinary viscose fibres.

The reactivity of viscose fibres under conditions of ethanolysis diminishes with increasing elongation. Celluloses possessing different reactivities and equal specific gravities have been found to be present in viscose fibres.

Cellulose hydrate subjected to dry grinding was found to possess properties analogous to ground wood cellulose.

PREPARATIONS OF SOME BLOCK POLYMERS AND INVESTIGATION OF THEIR PROPERTIES

B. M. Kovarskaia, L. I. Golubenkova, M. S. Akutin and I. I. Levandovskaia, Vysokomol. soedin. **1**: No. 7, 1042–1047, 1959.

In the report it has been shown that the physico-chemical properties of some block polymers obtained mechanochemically by means of special apparatus (laboratory modifier and continuous modifier) differ considerably from those of a mechanical mixture of the initial components.

CONTRIBUTION TO THE THEORY OF HIGH ELASTICITY OF RUBBERS

M. V. Volkenhtein, Iu. Ia. Gotlib and O. B. Ptitsyn, Vysokomol. soedin. **1**: No. 7, 1056–1062, 1959.

The cases for the disagreement of the "network" theory of high elasticity with experiment have been examined. The discrepancies have been found to be associated with forces due to correlation between configurations of the various chains and to bear an entropy rather than energy character. Modelling of the polymer by a mixture of Gaussian chains and rigid geometrical anistropic regions (packets) leads to stress-strain relations in harmony with experiment. It has thus been shown that intermolecular interaction in amorphous rubbers significantly affects their mechanical properties.

INVESTIGATION INTO THE WETTABILITY OF SOLID SURFACES BY POLYMERS

V. A. Kargin, M. B. Kostantinopolskaia, and Z. Ya. Berestneva, Vysokomol. soedin. **1**: No. 7, 1074–1076, 1959.

The wettability of various solid surfaces by polymers has been investigated. Most substances with surfaces differing in character have been shown not to be wetted by polymers. This points out to the completely different character of interaction between low molecular hydrocarbons and polymers and a solid surface. This is due to the fact that wetting of a solid surface by polymers is connected with change in their molecular configuration, requiring additional expenditure of energy. No analogy may therefore be drawn between the orders of magnitude of the energies of wetting of a solid surface by low molecular hydrocarbons and polymers.

STUDIES ON THE STRUCTURE AND PROPERTIES OF CARBOCHAIN POLYMERS IN DILUTE SOLUTIONS—IV. THE INTEGRAL AND DIFFERENTIAL HEATS OF SOLUTION AND DENSITIES OF THE POLYMERS

S. G. Zelikman, and N. V. Mikhailov, Vysokomol. soedin. **1**: No. 7, 1077–1085, 1959.

The integral and differential heats of solution of polyvinylchloride, polyacrylonitrile and their copolymers of various composition as well as of mixtures of the same composition of the polymers have been investigated. The densities of the polymers and of their mixtures have been determined. The lower densities of the copolymers in comparison with values

calculated on the basis of additivity and the increased integral heats of solution are explained by loosening of the copolymer structure owing to formation of intramolecular bonds between the nitrile carbon and the chlorine atom. In the case of mixtures (particularly for mixtures of the composition 13:87) a certain increase in density and decrease in the integral heats are observed, caused by the intensified molecular interaction between the different types of macromolecules.

SYNTHESIS AND SOME PROPERTIES OF POLYSTYRENE-ACRYLIC ACID GRAFT COPOLYMERS

P. V. Kozlov, M. M. Iovleva and N. A. Platé, Vysokomol. soedin. **1**: No. 7, 1100–1105, 1959.

GRAFT copolymers of polystyrene and acrylic acid with varying component ratios have been obtained by ozonizing polystyrene suspensions.

A study of the copolymer solubility showed it to diminish and become limited as a result of the grafting.

Investigation of the thermomechanical properties has confirmed the additivity for graft copolymers found earlier in the case of other systems.

THERMODYNAMIC STUDY OF COPOLYMER SOLUTIONS OF ETHYLENE GLYCOL AND TEREPHTHALIC AND SEBACIC ACIDS

P. V. Kozlov, M. M. Iovleva and L. L. Shyriaeva, Vysokomol. soedin. **1**: No. 7, 1106–1111, 1959.

THE change in solubility of copolymers of ethylene glycol and terephthalic and sebacic acids has been studied in relation to copolymer composition. The solubility was determined from the critical temperature of mixing of the copolymer with furfuryl alcohol.

Determinations were made of the integral heats of solution of the copolymers in *m*-cresol and furfuryl alcohol at 45°C.

The curves depicting the change in critical temperatures and the negative heat effects of solution were shown to have a minimum for the component ratio close to 1:1 bearing evidence of maximum solubility of such copolymers.

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RELATION BETWEEN STRUCTURE AND POLYMERIZATION CAPACITY OF STYRENE DERIVATIVES—II. POLYMERIZATION OF TRI- AND TETRA-SUBSTITUTED HALOGENMETHYLSTYRENES

A. F. Dokukina and M. M. Koton, Vysokomol. soedin. **1**: No. 8, 1129–1132, 1959.

CHLORODIMETHYLSTYRENE isomers and 2,3-dichloro-4,5-dimethylstyrene have been synthesized for the first time and their polymerization has been studied at 80, 100 and 120°C.

Incorporation of chlorine atoms in the dimethylstyrene molecule has been shown to increase its polymerization capacity.

In the case of the tri- and tetra-substituted compounds, the polymerization depends upon the nature of the substituting groups and on their position in the molecule.

PHYSICO-CHEMICAL STUDIES OF POLY-*p*-CARBOETHOXYPHENYLMETHACRYLAMIDE—I. ANOMALY IN THE INTRINSIC VISCOSITY-MOLECULAR WEIGHT RELATIONS OF POLY-*p*-CARBOETHOXYPHENYLMETHACRYLAMIDE

G. M. Chetyrkina, V. G. Aldoshin and S. Ia. Frenkel, Vysokomol. soedin. **1**: No. 8, 1133–1142, 1959.

THE incorporation of a carboethoxy group in the *para*-position of phenylmethacrylamide leads to sharp decrease in monomer reactivity and a 10-fold increase in the polymerization rate (G. M. Chetyrkina, G. A. Sokolova, M. M. Koton, Vysokomol. Soedin. 1, 248, 1959). A study in neutral solvents of some hydrodynamic characteristics of the polymer formed disclosed a number of anomalies that may be explained by the assumption of configurational rigidity in the poly-*p*-carboethoxyphenylmethacrylamide macromolecules. In order to prove that rigidity is due to intramolecular hydrogen bonding the intrinsic viscosity was measured in a competitive solvent system (dimethylformamide + 30 per cent formamide). All anomalies disappear in this solvent and the *p*-carboxyphenylmethacrylamide molecules behave as ordinary statistical coils.

It has been suggested that the configuration of macromolecules formed as the result of polymerization affects the rate of their growth.

ELECTRON MICROSCOPIC STUDY OF THE MECHANISM OF SINTERING OF POLYTETRAFLUOROETHYLENE (FLUOROPLAST-4)

V. A. Kargin, A. A. Gorina and T. A. Koretskaia, Vysokomol. soedin. **1**: No. 8, 1144–1147, 1959.

POLYTETRAFLUOROETHYLENE has been shown to possess a packet structure, i.e. the macromolecular chains are aggregated in packets which in turn are united into larger aggregates, producing secondary structure of a network character.

* English Abstracts reprinted from Vysokomol. soedin. 1: No. 8, 1959.

It has been found that in the sintering temperature range investigated (370–450°C) no melting that would lead to formation of an integrated mass takes place, nor is there even a partial increase in particle contact.

INFRA-RED SPECTRA OF GELATINE IN THE TEMPERATURE RANGE FROM −160 TO 250°C

M. A. Salimov and V. A. Pchelin, Vysokomol. soedin. **1**: No. 8, 1170–1177, 1959.

THE effect of temperature on gelatine films has been studied over a wide range of temperatures (−160, 25, 105, 250 and 250°C). On lowering the temperature to −160°C a small reversible change in the spectrum in observed, connected mainly with the vitrification process. At high temperatures (160, 200 and 250°) a number of reversible and irreversible changes in the spectrum occur. The reversible changes find expression in particular in a fall in intensity and disappearance of a number of absorption bands brough about by the partial destruction of hydrogen (largely *cis*-hydrogen) bonds with rise in temperature. Some of the bands in the spectra of the heated films are shifted towards the longer wave length region. This is interpreted as the results of diminution of the crystalline and growth of the amorphous phase. The reversible changes disappear on bringing the specimens to room temperature. The irreversible changes in the spectrum are manifested in an increase in the over-all absorption. They are interpreted as the result of an increase in the molecular network density of the gelatine xerogel.

SYNTHESIS OF NEW CELLULOSE AND OTHER POLYSACCHARIDE DERIVATIVES—II. THE SYNTHESIS OF AMINO ACID AMIDES OF ALGINIC ACID AND CARBOXYMETHYLCELLULOSE

Sun'-Tun, V. A. Derevitskaia and Z. A. Rogovin, Vysokomol. soedin. **1**: No. 8, 1178–1181, 1959.

A NEW class of polyuronic acid derivatives, viz., the glycine ε-aminocaproic acid and ξ-aminoethanthic acid amides of alginic acid and carboxymethylcellulose, has been synthesized for the first time.

ON THE MECHANISM OF CATALYTIC POLYMERIZATION OF CYCLIC DIMETHYLSILOXANES

V. N. Gruber and L. S. Mukhina, Vysokomol. soedin. **1**: No. 8, 1194–1199, 1959.

IT has been shown that at the basis of the catalytic polymerization of dimethylpolysiloxanes of cyclic structure by catalysts of acid character (conc. H_2SO_4, $FeCl_3$, $Al_2(SO_4)_3 \cdot 2H_2O$) lies an oxidation-reduction process with catalyst undergoes.

It appears that the catalysts proper are the oxidation-reduction systems formed in each particular case by the lower and higher oxide and peroxide forms of the catalyst.

A schematic diagram is presented of the oxidation-reduction systems for concentrated H_2SO_4 and $FeCl_3$.

Establishment of favourable conditions for oxidizing the reduced forms of the catalyst by passing oxygen through the polymerizing mass considerably increase the polymerization rate.

The mechanism of polymerization proposed by Pathnode and Wilcock does not effect the true character of the process.

COMPARATIVE STUDY OF HIGHLY ORIENTED CRYSTALLINE AND AMORPHOUS POLYMERS

V. I. Selikhova, G. S. Markova and V. A. Kargin, Vysokomol. soedin. **1**: No. 8, 1214–1226, 1959.

A COMPARATIVE X-ray study has been made of the ordering of polymers in the crystalline and amorphous states, as exemplified by highly oriented specimens of polyethylene, gutta percha, tetrafluorethylene vinylidenefluoride copolymer with 1:4 component ratio, and polyethyleneterephthalate. The amorphous state of the polymers (excepting polyethyleneterephthalate) was studied on the melts. Contraction and flow of the polymer chains at elevated temperatures was obviated by the use of rigid sheaths and irradiation of the specimens with γ-rays from a 60 Co source. An X-ray method for evaluating the degree of order of highly oriented films in the crystalline and amorphous states has been given. Calculation have been made of the distribution curves of tri-dimensional ordering sites with respect to the orientation angles and distribution curves of amorphous regions in the chains are determined from the X-ray data. High ordering has been shown to arise spontaneously in the process of phase transition.

ON THE KINETICS OF THE MECHANICAL DEGRADATION OF HIGH POLYMERS

B. V Pavlov, Vysokomol. soedin. **1**: No. 8, 1227–1235, 1959.

THE kinetics of the mechanodestruction of polymers are examined from the standpoint of disproportionation of the radicals formed. An equation has been derived, corelating the degree of polymerization with the mean elementary rate connstant of molecular destruction. It has been shown that with the aid of this equation from the form of the time dependence of the degree of polymerization one may derive a qualitative relationship between the elementary rate constant of destruction of a molecule and its length.

The correlations have been applied to an analysis of the experimental data on the shearing destruction of concentrated polymer solutions in a Mac-Kee consistometer and on destruction by means of ultrasonic waves.

STRUCTURAL CHANGES IN ORIENTED CRYSTALLINE AND AMORPHOUS POLYMERS IN THE SOFTENING TEMPERATURE REGION

V. I. Selikhova, G. S. Markova and V. A. Kargin, Vysokomol. soedin. **1**: No. 8, 1236–1241, 1959.

AN X-ray study of the structural changes taking place in oriented amorphous polymers (polyacrylonitrile, cellulose, propionmethacrylate, a number of synthetic rubbers) has been made over a wide range of temperatures including the the glass temperature and the region of the high elastic state of the polymers. The objective of the study was to compare the structural changes of oriented crystalline and amorphous polymers in the softening temperature region. Distribution curves of the chain sites with respect to the orientation angles have been plotted. In the case of amorphous polymers it was shown that no structural changes take place in the region of the softening temperatures. Comparison of the amorphous and crystalline polymer structures in the softening region showed that only phase transitions lead to spontaneous appearance of high order.

THERMAL STABILITY OF THE SULPHONOPHTHALENE-FORMALDEHYDE RESINS KU-5

N. G. Polianskii, V. I. Vyshnevskaia and Yu. Mizh-Mishin, Vysokomol. soedin. **1**: No. 8, 1249–1257, 1959.

IT has been found that heating the cation exchanger KU-5 in air is accompanied by the evolution of volatile products and decrease in exchange capacity and in relative swelling. The

principal volatile product evolved on moderately heating the resin (110°) was shown to be water. On stronger heating (185°) in addition to the water sulphur dioxide is evolved, indicating a decrease in the number of sulphoxyl groups of the polymer. With respect to capacity loss at 150 and 185° KU-5 approaches the other cation exchanger KU-1.

The relative changes in swelling and moisture sorbing capacities on heating KU-5 in air have been shown to considerably exceed the relative loss in exchange capacity per unit dry weight of resin. Because of this the thermal treatment leads to a rise in capacity when calculated on the basis of unit weight of the hydrated cation exchanger.

With respect to heating in water KU-5 has been found to be of greater stability than the sulphophenolformaldehyde resin KU-1, but inferior to the sulphonated-styrene-divinylbenzene copolymer KU-2. The principal cause of desulphination of KU-5 as well as of the other cation exchangers is the thermal hydrolysis reaction:

$$RSO_3H + H_2O \rightarrow RH + H_2SO_4$$

Despite the desulphonation of KU-5 on heating in water, its hydration capacity has been shown to increase. The concurrent increase in equivalent moisture sorption capacity leads to the conclusion that loosening of the lattice network of the polymer takes place on heating in water.

CARBOCHAIN POLYMERS AND COPOLYMERS—XII. EMULSION POLYMERIZATION OF VINYL COMPOUNDS IN THE PRESENCE OF TRIBUTYLBORON

H. S. Kolesnikov and L. S. Fedorova, Vysokomol. soedin. **1**: No. 8, 1266-1270, 1959.

A STUDY has been made of the effect of oxygen on the emulsion polymerization of acrylonitrile, methylmethacrylate and styrene. It has been qualitatively shown that in the polymerization of acrylonitrile in the presence of tributylboron and atmospheric oxygen, compounds of the type of peroxide are formed. In the polymerization of acrylonitrile atmospheric oxygen may be substituted by hydrogen peroxide.

Oxygen accelerates the polymerization of methyl methacrylate and styrene, which in contrast to acrylonitrile polymerize with tributylboron as catalyst in the absence of oxygen. However, without oxygen the yields are smaller. The oxygen effect is greatest in the polymerization of styrene.

A number of relationships has been established in the polymerization of acrylonitrile methylmethacrylate and styrene in the presence of tributylboron and atmospheric oxygen.

Following the abrupt fall in the initial stage of decomposition the degree of polymerization of cellulose hydrate continues to diminish gradually in the subsequent stages. In the entire process cellulose hydrate gives a higher yield of volatile liquids and a very low yield of levoglucosan as compared with the yields of these products in the second stage of decomposition of cotton cellulose.

It has been shown that the degradation of cotton cellulose is not due to the chemically changed elementary units.

Different relations in the formation of thermal decomposition products have been observed in the case of cotton cellulose and cellulose hydrate. It has been concluded that thermal decomposition of cotton cellulose in the second stage proceeds according to a chain mechanism, whereas that of cellulose hydrate takes place randomly along the chain.

ABSTRACTS FROM PAPERS PUBLISHED IN *VYSOKOMOLEKULIARNYE SOEDINENIIA* VOL. 1, NO. 9, 1959*

A STUDY OF THE ELECTRICAL PROPERTIES AND STRUCTURE OF LIQUID L,P-HEXAMETHYL (POLYPHENYLAMINOMETHYL) SILOXANES

G. E. Golubkov and K. A. Andianov, Vysokomol. soedin. 1: No. 9, 1273–1278, 1959.

A STUDY has been made of polyorganosiloxanes containing nitrogen in the organic radical. The compounds possess large dipole moments and dielectric constants. The incorporation of a phenyl radical shifts the relation region in the direction of higher temperatures.

THE EFFECT OF PLANE-RADIAL STRETCHING ON THE DIELECTRIC PROPERTIES AND STRUCTURE OF POLYETHYLENE

A. M. Arev, Vysokomol. soedin. 1: No. 9, 1279–1284, 1959.

THE capacitance of polyethylene at 50 Hz and 2×10^6 Hz frequencies and tg δ at 50 Hz have been determined in the plane-radial process of polyethylene. In addition X-ray diagrams have been obtained of the initial and stretched polymer.

The investigations carried out have shown that the plane-radial stretching of polyethylene causes the occurrence of recrystallization and re-orientation processess. As a result the structure and dielectric properties of the polymer undergo change.

It has been observed that the relatively part played by re-orientation is more important during plane-radial than during linear stretching.

ON THE AGGREGATE STATE OF LUMINESCENT ORGANIC COMPOUNDS IN POLYSTYRENE—II. DETERMINATION OF THE MOLECULAR WEIGHTS OF THE POLYMERIZATES

E. E. Baroni and V. M. Shoniia, Vysokomol. soedin. 1: No. 9, 1286–1286, 1959.

IT has been shown that the molecular weight of polystyrene polymerized in the presence of luminescent organic additions of varying chemical structures, is independent of the presence of the additions.

SOME FEATURES OF THE STRENGTHENING ACTION OF CARBON BLACKS FOLLOWING FROM THE TEAR BEHAVIOUR OF FILLED RUBBERS

A. I. Lukomskaia, Vysokomol. soedin. 1: No. 9, 1287–1294, 1959.

CARBON black filled natural (NK) and synthetic (SKB, SKS-30) rubber vulcanizates under certain conditions yield knotty tears. Within the temperature limits $-40°$ to 100°C and

* English abstracts reprinted from vysokomol. soedin. 1: No. 9, 1959.

rates from 50 to 1000 mm/min SKB and SKS-30 vulcanizates with thermal black or a small amount of channel black as well as filled NK vulcanizates have only one temperature-rate region of knotty tear. With high channel carbon content SKB and SKS-30 vulcanizates yield two knotty tear regions.

It has been suggested that one of the knotty tear regions is connected with the presence in the vulcanizates of the carbon black particles, whereas the other with carbon black chain structures.

MECHANISM OF THE THERMAL DECOMPOSITION OF CELLULOSE IN VACUUM —I. COMPARATIVE STUDY OF THERMAL DECOMPOSITION OF COTTON CELLULOSE AND OF CELLULOSE HYDRATE

O. P. Golova, R. G. Krylova and N. N. Nikolaeva, Vysokomol. soedin. **1**: No. 9, 1295–1304, 1959

In order to elucidate the mechanism of thermal decomposition of cellulose with formation of β-1,6-anhydro-1,5, glucopyranose a comparative study of the relations governing the formation of volatile products and of the changes in properties of the cellulose itself for two of its structural modifications has been made.

The experimental results indicate that decomposition of cotton cellulose proceeds in two stages. Decomposition of the first 2–4 per cent is accompanied by a sharp fall in the degree of polymerization. On decomposition of the following 70–80 per cent the degree of polymerization remains constant.

When the first 10–20 per cent cellulose is decomposed the process proceeds with little levoglucosan formation and with large yield of volatile products. In the subsequent 50–70 per cent decomposition, the levoglucosan yield is practically constant.

MECHANISM OF THE THERMAL DECOMPOSITION OF CELLULOSE IN VACUUM —II. INHIBITION OF THE THERMAL DECOMPOSITION

O. P. Golova, R. G. Krylova and I. I. Nikolaeva, Vysokomol. soedin. **1**: No. 9, 1305–1308, 1959.

The thermal decomposition of cotton cellulose in vacuum has been shown to be capable of inhibition by products of the concurrent decomposition of glucose. The active fragments of the glucose molecules do not participate in the decomposition process of the cellulose macromolecules in the initial stage. Inhibition is accompanied by change in direction of the process, products of the more far-going C—C bond cleavage being formed.

MECHANICAL VITRIFICATION AND THE ACTIVATION ENERGY OF RUBBER-LIKE POLYMERS

G. M. Bartenev and V. D. Zaitseva, Vysokomol. soedin. **1**: No. 9, 1309–1318, 1959.

The results of investigations of mechanical vitrification of a broad variety of rubbers over the range of deformation frequencies 0·1–1000 sec^{-1} have been presented. Based on the mechanical model of rubber with a single relaxation time and on experimental data the energy of activation of molecular rearrangements for various rubbers has been calculated and compared with the mechanical vitrification temperature.

MOLECULAR ORDERING OF POLYMERS PRECIPITATED FROM SOLUTIONS

L. A. Igonin, A. V. Ermolina, Yu. V. Ovchinnikov and V. A. Kargin, Vysokomol. soedin. **1**: No. 9, 1327–1332, 1959.

CHANGES in the molecular ordering of polyvinylchloride, polymethylmethacrylate and methacrylate-methacrylic acid copolymer in the process of heat pressing of specimens precipitated from solutions have been studied. A study has also been made of the change in character of the electronogram on thermal treatment of thin polymer films obtained from the solutions.

Based on the results obtained it has been concluded that the initial polymers differ in ordering from the precipitated ones. The latter preserves to a certain extent the low ordering characteristics of solutions. On annealing such polymers ordering of the molecular chains takes place accompanied by characteristic changes in the physical properties.

A STUDY OF THE PRESSURE SINTERING OF POLYMERS—I. REGION OF PRODUCTION OF TRANSPARENT SPECIMENS

S. A. Arzhakov, E. E. Rylov and B. P. Shtarkman, Vysokomol. soedin. **1**: No. 9, 1351–1356, 1959.

IN the compaction of powdered polymethylmethacrylate and methylmethacrylate-acrylic acid copolymers curves in lgP–T co-ordinates have been plotted, marking regions of formation of transparent specimens.

The shape and position of the curves depends upon the number of polar groups in the polymer and plasticizer and upon the molecular weight. The presence of an upper branch is explained by the stiffening of polymer chains under large pressures, whereas the position and shape of the lower branches is connected with the modulus and viscosity of the polymers.

A STUDY OF THE PRESSURE SINTERING OF POLYMERS—II. THE REGION OF TRUE COMPACTION

S. A. Arzhakov, E. E. Rylov and B. P. Shtarkman, Vysokomol. soedin. **1**: No. 9, 1357–1360, 1959.

IN the compaction of polymethylacrylate and methylmethacrylate—methacrylic acid copolymer powders—conditions have been found, when within the lgP–T curves the preparations undergo little change in their linear dimensions on heating above the T_g temperature.

It has been shown that the specimens exhibiting no change in linear dimensions on heating above T_g may be prepared only under conditions when flow of the polymer takes place.

POLYMERS WITH CONJUGATED BONDS IN THE MACROMOLECULAR CHAINS—II. MAGNETIC AND SOME OTHER PROPERTIES OF POLYARYLVINYLENES

A. A. Berlin, L. A. Blumenfeld, M. I. Cherkashin, A. E. Kalmanson and O. G. Selskaia, Vysokomol. soedin. **1**: No. 9, 1361–1363, 1959.

SOME physico-chemical and physical properties of a new class of polymers, polyaryl vinylenes, have been investigated. Thermal stability has been shown to increase parallel with increase in degree of polymerization, which is accompanied by increase in length of the chain containing the conjugated double bonds and a darkening of the colour even to blackness.

Beginning with a certain degree of polymerization, the polymers reveal magnetic resonance signals of which the intensity corresponds to concentrations of unpaired electrons from 10^{17} to 10^{19} per g specimen, depending upon the degree of polymerization.

PREPARATION OF GRAFT COPOLYMERS – IV. THE GRAFTING OF VINYL MONOMERS TO POLYAMIDES

V. V. Korshak, K. K. Mozgova and M. A. Shkolina. Vysokomol. soedin. **1**: No. 9, 1364–1368, 1959.

FURTHER studies on the method of obtaining graft copolymers from polyamides and vinyl monomers with the use of ozone as activator have been made.

As objects of the present study served films and fibres of the polyamides: capron, anide-G-669, enanth and the monomers: styrene, acetate, acrylonitrile, and methylmethacrylate.

The results of the study showed that the grafting of vinyl monomers to the polyamides depends upon the reactivity of the initial monomer and the degree of orientation of the films and fibres of the polyamides.

POLYMERIZATION OF VINYL DERIVATIVES OF DIPHENYL, DIPHENYLOXIDE AND DIPHENYLSULPHIDE

P. A. El'tsova, M. M. Koton, O. K. Mineeva and O. K. Surnina, Vysokomol. soedin. **1**: No. 9, 1371–1373, 1959.

A KINETIC study has been made of the polymerization of *o*-and *p*-vinyldiphenyl, *p*-vinyldiphenyloxide and *p*-vinyldiphenylsulphide.

The activation energies of the compounds have been determined. The dipole moments of *p*-vinyldiphenylsulphide and *p*-vinyldiphenyloxide have been measured.

The thermal stability and the solubility of the polymers obtained have been determined.

AN INVESTIGATION INTO THE DIELECTRIC LOSSES AND ULTRASONIC WAVE ABSORPTION IN POLYPROPYLENE

B. I. Sazhin, V. S. Skurikhina and Yu. A. Il'in, Vysokomol. soedin. **1**: No. 9, 1383–1389, 1959.

IN the paper the results are presented of measurement of the slope of dielectric losses at temperatures ranging from – 100 to 150°C and frequencies 400–10^{10} Hz and of the attenuation coefficient of longitudinal ultrasonic waves in propylenes of varying densities.

The data show that the observed dielectric and mechanical relaxation losses are associated with segement mobility in the amorphous phase of polypropylene.

THERMOMETRY AS A METHOD OF STUDYING POLYMERIZATION KINETICS – I. PRINCIPLES OF THE METHOD AND THE EXPERIMENTAL SET-UP

G. V. Korlev, B. V. Pavlov and A. A. Berlin, Vysokomol. soedin. **1**: No. 9. 1396–1402, 1959.

A DESCRIPTION has been given of an experimental arrangement for thermometric measurements (including thermistor and the self-recording bridge MS-1), used for determining the rate of polymerization in the course of the reaction.

MOLECULAR INTERACTION AND SEGMENT ANISOTROPY OF CHAIN MOLECULES IN SOLUTION

V. N. Tsvetkov, V. E. Bychkova, S. M. Savvon and I. K. Nekrasov, Vysokomol. soedin. **1**: No. 9, 1407–1415, 1959.

THE double refringence and viscosity of poly*iso*butylene (PIB) solutions in benzene and of poly(3,4-dichlorostyrene (PDCS) in tetrabromethane in the vicinity of the Flory point have been investigated.

The experiments have shown that long range interaction leading to considerable augmentation of macromolecular dimensions in solution has practically no effect on their segment anisotropy and hence change in the distribution function of the segments does not affect the length of the macromolecules.

The value obtained for the segment anisotropy for PIB and PDCS permits of a number of inferences as to the geometry and flexibility of the molecular chains.

STUDY OF THE POLYMERIZATION OF STYRENE ON A ZIEGLER TYPE CATALYST WITH THE AID OF THE MOLECULAR BEAM METHOD

V. A. Kabanov, V. P. Zubov and V. A. Kargin, Vysokomol. soedin. **1**: No. 9, 1422–1427, 1959.

TITANIUM trichloride in ultimately disperse form or of highly defective structure has been found with the aid of the molecular beam method to be capable of initiating the quick non-stereospecific low temperature polymerization of styrene in the absence of a cocatalyst. The presence of triethylaluminium as the fourth component in the system, ultimately dispersed $TiCl_3$-monomer-solvent, does not hinder the rapid non-stereo-specific polymerization. The slow, stereospecific polymerization of styrene in the presence of $AlEt_3$ can take place provided the monomer is introduced in the reaction mixture after formation of $TiCl_3$ crystals. The method developed of microscopic observation of the processes taking place in the system: styrene-$TiCl_4$-AlE_2-solvent, depending upon the order of mixing the components. It has been shown that stereospecific polymerization may take place if the interaction between $TiCl_4$ and $AlEt_3$ leading to the formation of lower titanium chlorides and their crystallization takes place in the absence of the monomer. If the lower chlorides are precipitated in the presence of the monomer the rapid non-stereospecific reaction takes place.

A STUDY OF THE ELECTROCHEMICAL PROPERTIES AND THE SHAPES OF THE MOLECULES OF ETHYLENESULPHIDE AND ACID COPOLYMERS

V. A. Kargin, S. Ia. Mirlina and A. D. Antipina, Vysokomol. soedin. **1**: No. 9, 1428–1437, 1959.

A STUDY has been made of the effect of electrostatic interaction on the shape of the copolymer chains of weak and strong acids by investigating the viscosity, potentiometric titration values, electroconductivity, conductometric titration values and by electron-miscoscopic studies of aqueous solutions of ethylenesulpho- and acrylic acid copolymers and polyethylenesulphoacid.

Based on the investigations it has been concluded that copolymers of weak and strong acids change the shape of their chains with change in charge owing to the coiling and uncoiling of the macromolecular chains due caused electrostatic interaction.

The change in shape of the chains takes place in conformity with free energy changes.

With decrease in acrylic acid content of the copolymer and in solutions of pure polyethylenesulphoacid only ionic pairs are formed leading to chain coiling since the ionic strength of the solution is not enough for the formation or more complex associates and for uncoiling of the chain.

EFFECT OF PRESSURE ON THE GLASS TEMPERATURE OF POLYMERS

S. A. Arzhakov, E. E. Rylov and B. P. Shtarkman, Vysokomol. soedin. **1**: No. 9, 1438, 1959.

THE temperature dependence of polymethylmethacrylate has been studied at various external pressures. It has been shown that beginning with 500kg/cm² a sharp increase is observed in the glass temperature of the polymer, connected, evidently, with the fact that under such pressures the free intermolecular volume is exhausted.

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V. A. KABANOV, G. B. SERGEYEV, V. P. ZUBOV and V. A. KARGIN: Electron paramagnetic resonance study of polymerization in the acronitrile- magnesium system obtained by molecular beam condensation

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